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WADC TECHNICAL REPORT 53-126

AD 0014907

ELEVATED TEMPERATURE-RESISTANT MODIFIED EPOXIDE RESIN ADHESIVES FOR METALS

M. NAPS

SHELL DEVELOPMENT COMPANY

SEPTEMBER 1953

Statement A
Approved for Public Release

WRIGHT AIR DEVELOPMENT CENTER

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WADC TECHNICAL REPORT 53-126

ELEVATED TEMPERATURE-RESISTANT MODIFIED EPOXIDE RESIN ADHESIVES FOR METALS

M. Naps

Shell Development Company

September 1953

Materials Laboratory
Contract No. AF 33(600)-6514
RDO No. 614-11

Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

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FOREWORD

This report was prepared by the Shell Development Company, under USAF Contract No. AF 33(600)-6514. The contract was initiated under Research and Development Order No. 614-11, "Structural Adhesives", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt B. W. Andrews acting as project engineer.

ABSTRACT

A metal-to-metal adhesive which is useful at temperatures up to 500°F has been developed. The adhesive, designated as Formulation No. 422, is a one-package system composed of EPON 1001 resin, a liquid phenolic resin, Plyophen 5023, and dicyandiamide as the curing agent. Aluminum dust is used as the reinforcing filler. The adhesive is cured at contact pressure and at elevated temperature (330°F).

Bonds to aluminum from adhesive Formulation No. 422 have a shear strength of 2100 psi at room temperature and 1400 psi at 500°F. After 200 hours aging at 500°F adhesive shear strength is mediocre (ca 200 psi). Bond strength is, however, 1000 psi after approximately 70 hours aging at 500°F. Aging the adhesive bonds for 200 hours at 400°F reduces the shear strength (at 400°F) from 1750 psi to 1340 psi. Cycling the adhesive bonds between room temperature and elevated temperatures (up to 500°F) for fifty times has had no apparent effect upon the bond strength.

Adhesive Formulation No. 422 is used as a pliable tape, preferably supported on a glass fabric carrier. The adhesive must be stored under refrigeration; storage life at 40°F is about one month.

Systematic variation of the concentration of the components of the adhesive led to the development of the following formula (parts by wt): 33 EPON 1001 + 67 Plyophen 5023 + 100 aluminum dust + 6 dicyandiamide. Higher EPON 1001 resin content decreased hot strength; higher phenolic content increased brittleness and decreased thermal resistance upon aging. Either lower amounts of filler or curing without dicyandiamide reduced adhesive shear strength, especially at room temperature.

The conclusions summarized above represent the status of the work at this writing, but since the work is continuing these conclusions are only tentative. The adhesive 422 is considered an experimental product, and further work is indicated before the adhesive becomes a commercial product.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. E. SORTE
Colonel, USAF
Chief, Materials Laboratory
Directorate of Research

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Introduction

This is a progress report on the development of a high temperature metal to metal adhesive. The research is not yet complete, and the summary of the results are therefore inconclusive, but we shall summarize the progress which has been made to date.

The basic task of this project is to develop an EPON resin metal to metal adhesive which is useful at temperatures up to 500°F.

Our work has begun by exploring five lines of endeavor: (a) silicon modified EPON resins, (b) EPON resins with a high epoxide content, (c) co-reactants such as other resins as curing agents, (d) reinforcing fillers, and (e) better curing agents for EPON resins.

After pursuing all these lines for a period, it became apparent that one of the combinations of an EPON resin and a phenolic resin formed the basis of an adhesive which approached the target properties. Our attention was, therefore, concentrated on adhesives based on this combination. The work on these formulations finally lead to a compound 422, that number being the four hundred and twenty second combination tested up to the date of its adoption. The studies of systematic variations around this formula, and the evaluations of them make up the subject of this report.

Description of Adhesive Formulation No. 422

An adhesive composition based on a combination of solid EPON 1001 resin and a liquid phenolic resin of high methylol content, Plyophen 5023, was the most promising high temperature metal-to-metal adhesive developed under Contract AF 33(600)-6514. The basic task was the development of an adhesive which would maintain 1000 psi at temperatures up to 500°F. The adhesive bond formed by the co-reaction of the EPON resin and the phenolic resin at a 33/67 polyepoxide/phenolic resin ratio approaches the target properties of the contract. Maximum bond strength was obtained by curing the resin combination with _ca_ 6 phr[a] dicyandiamide and employing 100 phr aluminum dust as a reinforcing filler. The adhesive is used most conveniently in the form of a pliable tape (thickness _ca_ 10 mils) which is placed between the cleaned aluminum surfaces. The adhesive bond is cured for one-half hour at 330°F at contact pressure.

The adhesive is prepared by combining the resins at elevated temperature to form a homogeneous blend and then adding the filler and dicyandiamide. It is important to control the temperature and heating period to avert pregelation of the adhesive. (Premature gelation is apt to occur because Plyophen 5023 cures upon heating and also reacts with the epoxide resin.) Adhesive batches of 0.1 to 1.0 lb have been prepared successfully by the following procedure:

1. Melt EPON 1001 resin in a water bath at 175° to 190°F.
2. Add Plyophen 5023 with stirring, gradually increasing the water bath temperature to 210°F.
3. Add aluminum dust and dicyandiamide with stirring.
4. Heat the mixture 10 to 12 minutes. The total heating period after the addition of the phenolic resin should not be greater than 15 minutes.

The adhesive prepared in the above manner is fluid at _ca_ 190°F and can be used immediately, if desired. The hot melt paste is spread on the metal surface and scraped to a thickness of _ca_ 5 mils. Application is facilitated by preheating the metal to _ca_ 250°F. The flow of the adhesive is excellent at curing conditions and consequently thin glue lines of 3 to 4 mils can be obtained without scraping off the excess adhesive. The pot life of the hot melt adhesive is 20 to 40 minutes depending upon the age of the phenolic resin and the preheating period used in the preparation of the adhesive. Minimum heating periods and fresh Plyophen 5023 resin favor longer pot life.

The most satisfactory method of handling the adhesive is in the preparation of a supported tape by coating a light, open-weave glass fabric (e.g. grade 106) with the hot melt at _ca_ 190°F. The fabric is completely

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a) Throughout this report the abbreviation "phr" is used to designate the concentration of all types of additives as parts by weight per hundred parts of _total_ resin.

impregnated with the adhesive mixture. A supported tape of ca 10 mils thickness has given good adhesive bonds. Cellophane or polyethylene is used as a separator sheet.

Unsupported adhesive tape can also be fabricated directly from the hot melt paste. The adhesive is poured onto cellophane and chilled (preferably with refrigeration) to form a semi-plastic mass. A film of 10 to 14 mils is then formed by cold rolling or by pressing.

The adhesive is quite perishable and must be stored under refrigeration at 40°F or lower. The storage life at room temperature is one to three days. Tapes stored for one month at 40°F have shown no evidence of deterioration. After three months' refrigeration, however, the performance is poor, especially at 500°F. Shear strength at 500°F for bonds prepared with the adhesive tape aged three months is about 40% of the value obtained with fresh material.

The performance of the high temperature adhesive (Formulation No. 422) in metal-to-metal bonds is described in the following section of this report.

Properties of Adhesive Bonds from Formulation No. 422

Aluminum-to-aluminum adhesive bonds from Formulation No. 422 have shown promising high temperature performance and good strength retention throughout a temperature range of -70° to 500°F. Complete adhesive strength data are summarized in Table 1. The effect of the test temperature upon shear strength is shown graphically in Figure 1 and is also given below.

Test Temperature	Tensile Shear Strength, psi
-70°F	2265
Room temperature	2110
300°F	1835
400°F	1755
500°F	1370

The degree of strength retention after long time (200 hrs) aging of the unstressed adhesive bonds at elevated temperatures is excellent at 300°F and 400°F and mediocre for bonds aged at 500°F. The data follow:

	Shear Strength, psi
Aged 200 hrs at 300°F, tested at 300°F	2345
Aged 200 hrs at 400°F, tested at 400°F	1340
Aged 200 hrs at 500°F, tested at 500°F	ca 200

Deterioration in adhesive strength upon aging at 500°F was quite rapid. After 50 to 70 hours aging shear strength at room temperature was ca 1000 psi. The effect of exposure time at 500°F upon adhesive shear strength is shown graphically in Figure 2.

 (Figures 1 and 2 follow)

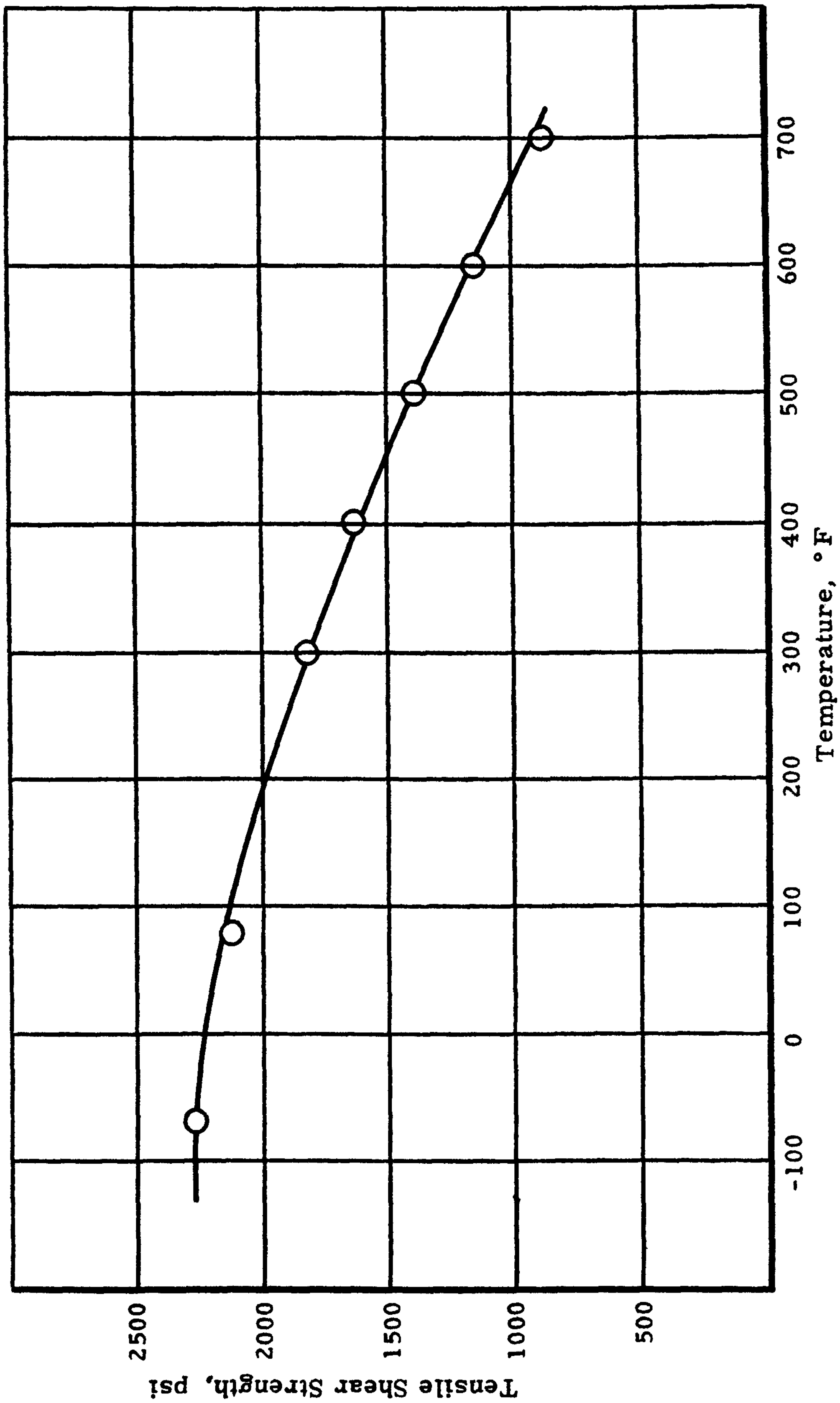

Figure 1. EFFECT OF TEMPERATURE UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE FORMULATION NO. 422

Cure: one-half hour at 330° F

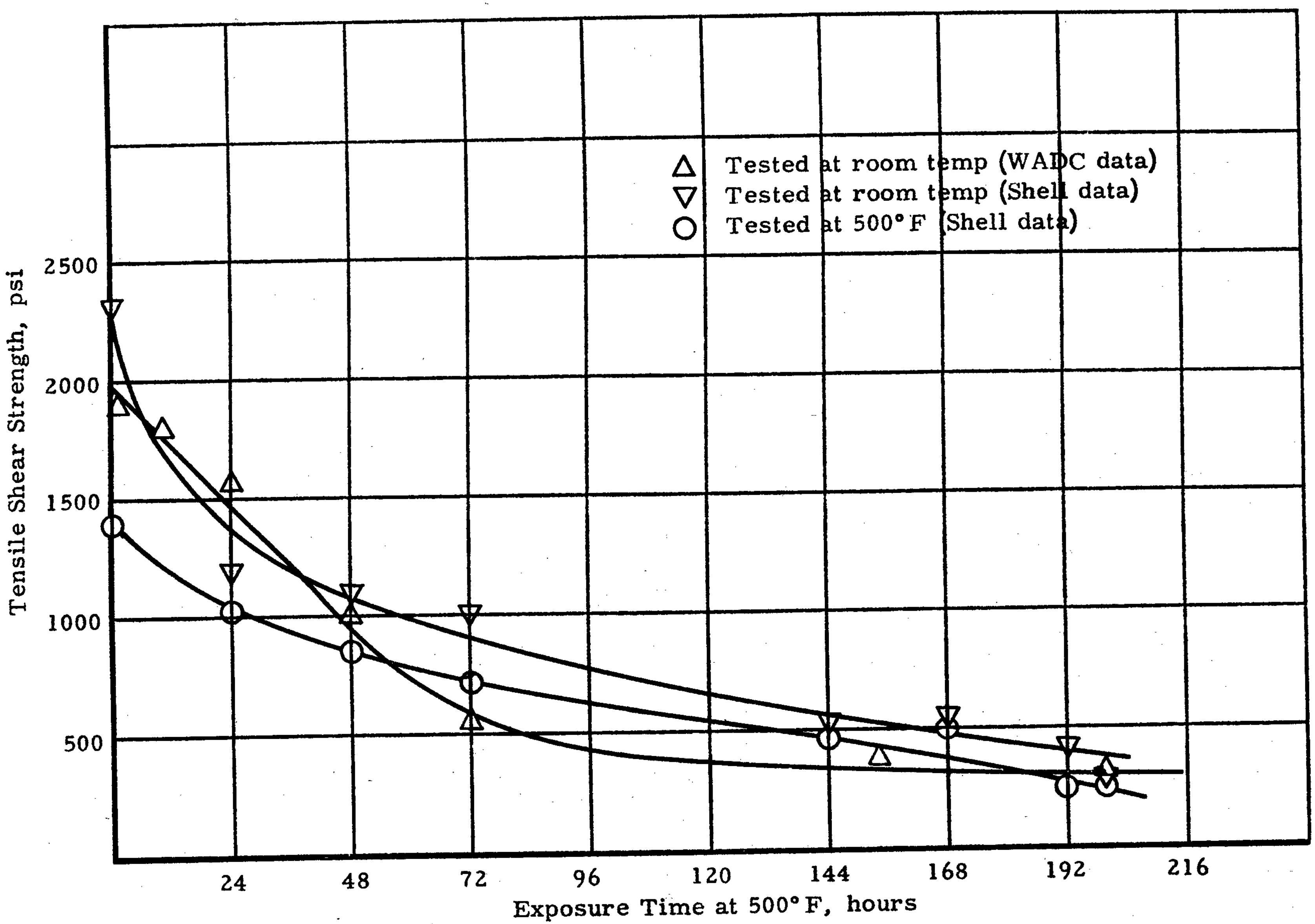

Figure 2. EFFECT OF AGING AT 500° F UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE FORMULATION NO. 422

Tests on the effect of cycling the adhesive bonds between room conditions and elevated temperatures indicated that strength retention was excellent after cycling fifty times between room temperature and the test temperatures 300°F, 400°F and 500°F. Shear strength after 50 cycles, and tested at the top cycle temperature, was 2180 psi at 300°F, 2000 psi at 400°F and 1255 psi at 500°F. The test results are summarized in Table 2 and are also plotted in Figure 3.

Fluid exposure tests on adhesive bonds from Formulation No. 422 indicated that the resistance to water, salt spray and various solvents met the requirements of U.S.A.F. Specification 14164. Shear strength at room temperature was at least 2000 psi after 30 days exposure to salt spray and tap water and 8 days immersion in ethylene glycol, anti-icing fluid, hydraulic oil and hydrocarbon fluid. The test results are given in Table 3.

Adhesive glue lines from Formulation No. 422 are somewhat brittle and low in extensibility. These characteristics are reflected in the bend strength and peel performance of the adhesive bonds and it is recognized that improvement in these properties is desirable. The bend strength at room temperature is ca 112 lbs.

The use of a supported tape with a glass fabric carrier (or the insertion of glass fabric in the glue line) appears to improve adhesive bond strength. A limited number of experiments conducted in these Laboratories and by the Materials Laboratory, Wright Air Development Center, indicate that tensile shear strength at room temperature and at 500°F was increased ca 10% and the bend strength increased ca 23% when glass fabric was used in the glue line. The light weight, open-weave fabric (grade 106) appears to be preferable to the heavier fabric (grade 667) or the closely-woven fabric (grade 113). The data follow:

	Plain	With Glass Fabric
Tensile shear strength at room temp, psi		
Shell data	2175	2125 (fabric 667)
Shell "	2175	2000 (fabric 113)
WADC "	2270	2400 (fabric 106)
Tensile shear strength at 500°F, psi		
Shell data	1385	1415 (fabric 667)
Shell "	2175	1295 (fabric 113)
WADC "	1700	1950 (fabric 106)
Bend strength at room temp, lbs		
Shell data	112	145 (fabric 667)

A preliminary evaluation of the strength of adhesive bonds to 301 stainless steel showed that the shear strength to steel (cleaned with concentrated hydrochloric acid) is as great or slightly greater than the strength to clad aluminum alloy. Shear strength test values were 2345 to 2900 psi at room temperature and 1280 to 1665 psi at 500°F. The experimental data are summarized in Table 4. Illustrative data follow:

 (Figure 3 follows)

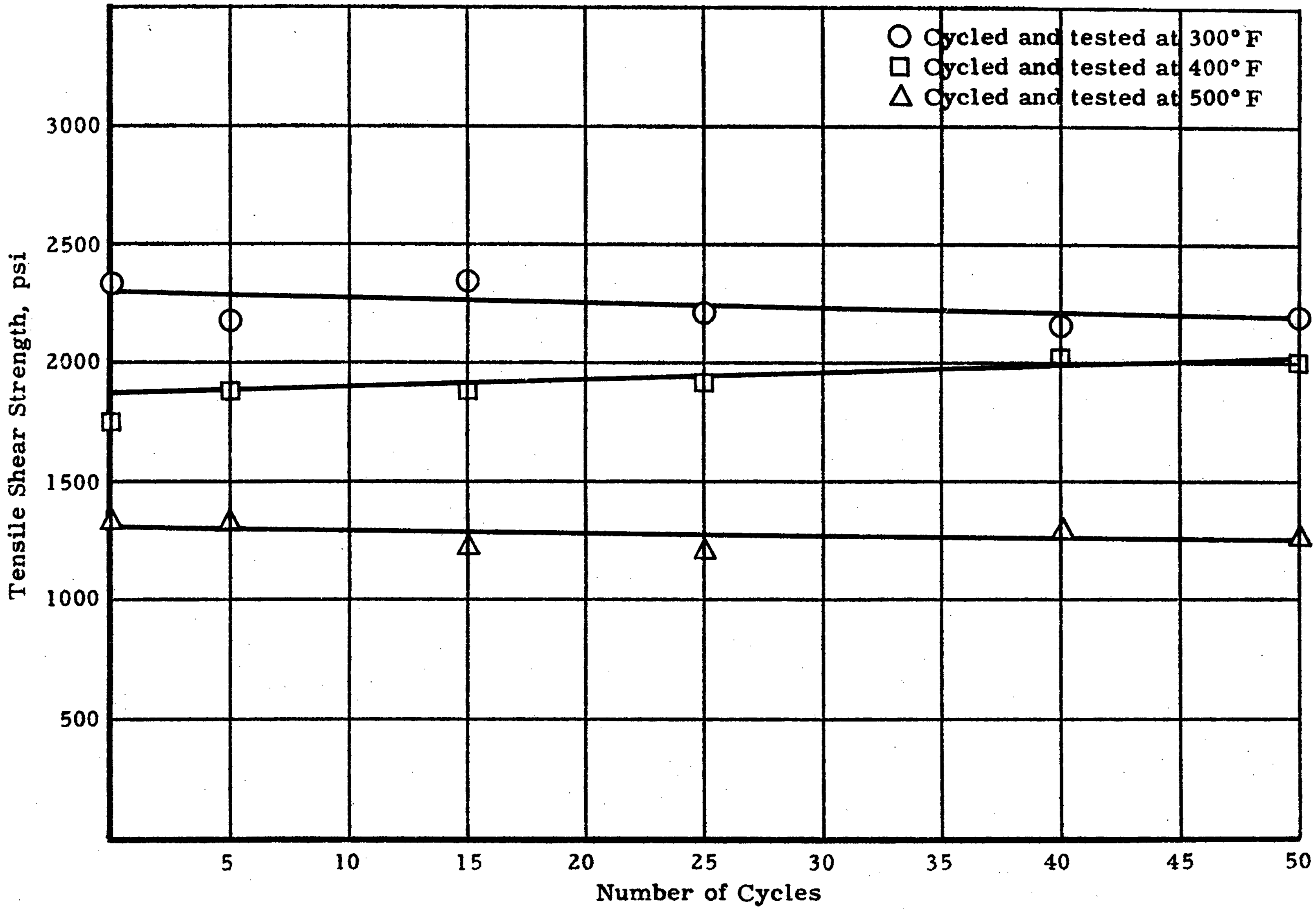

Figure 3. THE TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM FORMULATION NO. 422 AFTER CYCLING AT ELEVATED TEMPERATURES
Cure: one-half hour at 330° F

	301 Steel	Alclad 24S-T3
Tensile shear strength at room temp, psi		
Shell data	2725	2015
Shell "	2900	2165
WADC "	2345	2270
Tensile shear strength at 500°F, psi		
Shell data	1280	1180
Shell "	1600	1150
WADC "	1665	1700

Formulation Studies of Adhesives Based on Combinations of EPON 1001 Resin and Plyophen 5023

EPON 1001/Plyophen 5023 Resin Ratio

The effect of EPON 1001/Plyophen 5023 resin ratio upon the bond strength of high temperature adhesives was studied briefly for formulations which contained 60 phr aluminum dust filler (see Table 5) and more extensively for formulations which contained 100 phr aluminum dust filler (see Table 6). Hot melt compositions were prepared with 67/33, 50/50, 33/67, 25/75, 20/80, 10/90 and 0/100 EPON 1001/Plyophen 5023 resin ratios. Cure was one-half hour at 330°F with 5 phr dicyandiamide. Shear strength tests were conducted at room temperature and at 500°F before and after 200 hours aging at 500°F. The test results for one of the experiments are presented graphically in Figure 4. Bend strength tests were also conducted on the unaged adhesive bonds.

Room temperature shear strength of the unaged bonds decreased progressively with increasing phenolic content from 2585 psi for the 67/33 EPON 1001/Plyophen 5023 resin ratio to 1240 psi for the 100% phenolic adhesive. Shear strength at 500°F for the unaged adhesive bonds was mediocre at high EPON 1001 resin concentrations (67%) and appeared to be optimum at an epoxide resin content of 20 to 33%. The data follow:

EPON 1001/Plyophen 5023 Resin Ratio	Tensile Shear Strength, psi at 77°F	at 500°F
67/33	2585	550
50/50	2265	1065
33/67	2100	1380
25/75	2040	1805
20/80	1640	1705
10/90	1675	1510
0/100	1240	1270

The shear strength of adhesive bonds which were aged 200 hours at 500°F decreased progressively with increasing phenolic content. The shear strength was 465 psi for the adhesive based on 67/33 EPON 1001/Plyophen 5023 and zero for bonds prepared from 100% phenolic resin. Strength retention was maximum (ca 22%) for the 33/67 EPON 1001/Plyophen 5023 resin ratio. The data follow:

(Figure 4 follows)

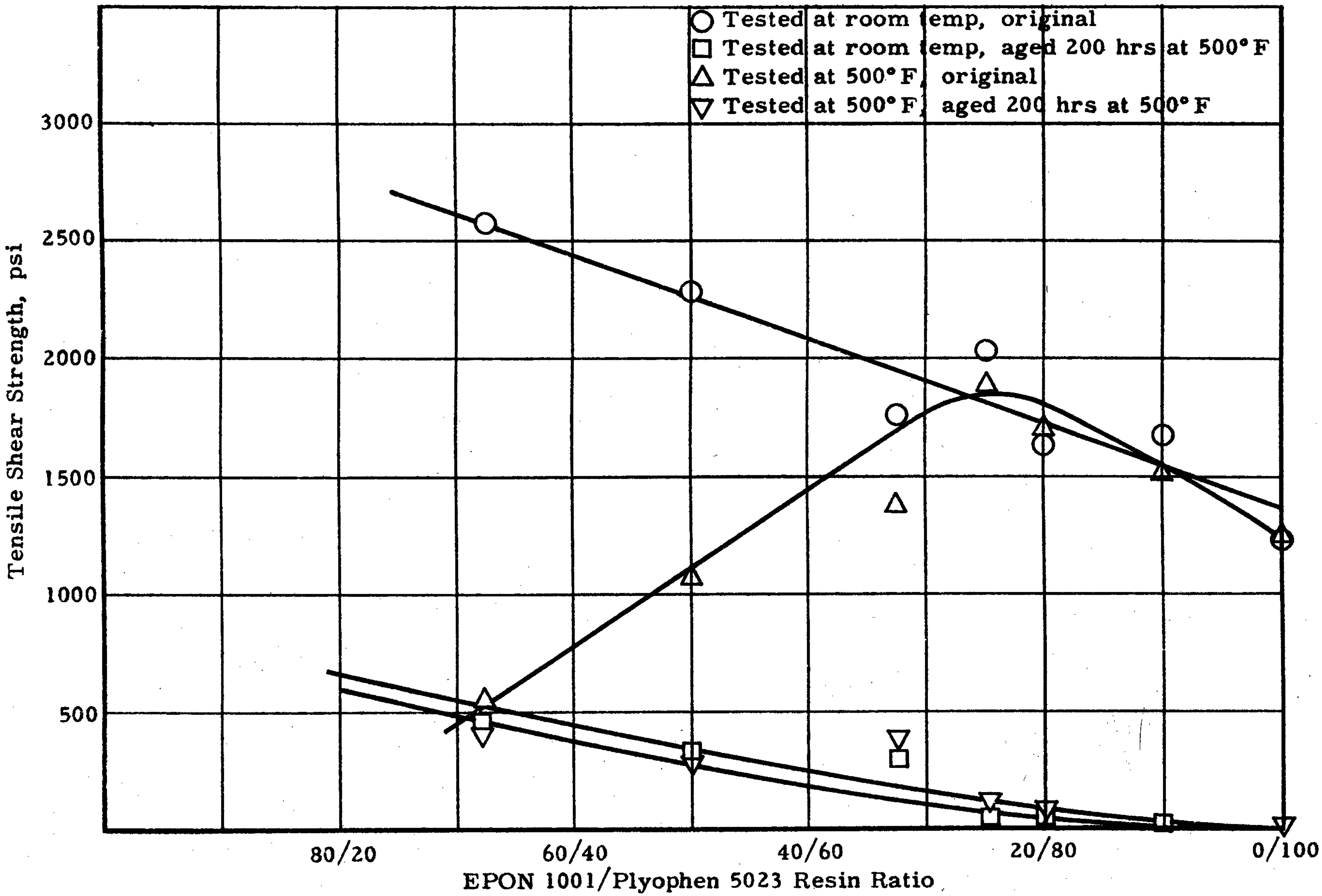

Figure 4. EFFECT OF EPON 1001/PLYOPHEN 5023 RESIN RATIO UPON TENSILE SHEAR STRENGTH
Constants (parts by wt): 100 aluminum dust + 5 dicyandiamide
Cure: one-half hour at 330° F

EPON 1001/Plyophen 5023 Resin Ratio	Tensile Shear Strength after 200 Hrs at 500°F at 77°F	at 500°F
67/33	465	465
50/50	345	305
33/67	300	375
25/75	50	55
20/80	50	50
10/90	0	10
0/100	50	0

The bend test results for the series of varying EPON 1001/Plyophen 5023 resin ratios were erratic and no correlation was demonstrated. Bend strength was 84 to 148 lbs; a high EPON 1001 resin content appeared to be favorable.

The effect of polyepoxide/phenolic resin ratio upon adhesive bond strength was also studied for combinations of EPON 864 resin and Plyophen 5023. EPON 864 resin, which has a lower softening point than EPON 1001, was evaluated because it affords some minor advantages in adhesive preparation and properties, particularly storage life. The properties of the two epoxy resins follow:

	Average Molecular Weight	Softening Point, °F
EPON 864	710	104-113
EPON 1001	900	149-167

Hot melt adhesives were prepared with 67/33, 50/50, 33/67, 25/75, 20/80, 10/90 and 0/100 EPON 864/Plyophen 5023 resin ratios using aluminum dust filler and dicyandiamide as the curing agent. The experiments are summarized in detail in Table 7. In one series of experiments shear strength tests were conducted at room temperature and at 500°F before and after the adhesive bonds were aged for 200 hours at 500°F. These data are plotted in Figure 5.

Room temperature shear strength decreased progressively from a value of 2675 psi to 1240 psi as the Plyophen 5023 content was increased from 33 to 100%. The initial hot strength (500°F) was maximum (1370 psi to 1605 psi) at a phenolic content of 67 to 80%. The shear strength at room temperature and at 500°F of aged bonds decreased progressively from ca 400 psi to zero as the resin ratio was increased from 67/33 to 100% Plyophen 5023. In general, the performance of EPON 864-Plyophen 5023 adhesives of varying resin ratio was comparable to that of EPON 1001-Plyophen 5023 described previously. The data follow:

(Figure 5 follows)

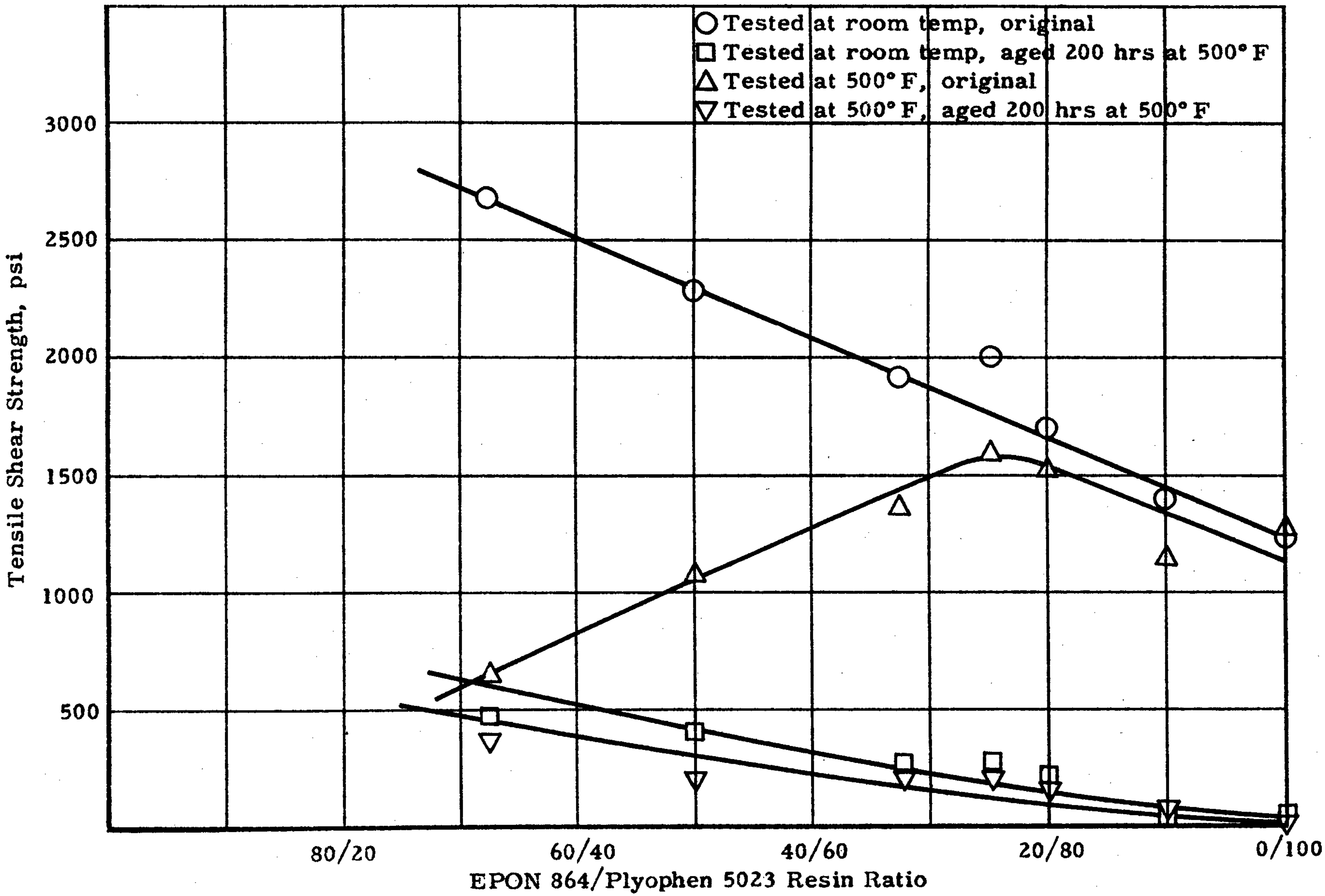

Figure 5. EFFECT OF EPON 864/PLYOPHEN 5023 RESIN RATIO UPON TENSILE SHEAR STRENGTH

Constants (parts by wt): 100 aluminum dust + 5 dicyandiamide

Cure: one-half hour at 330° F

For unaged adhesive bonds

EPON 864/Plyophen 5023 Resin Ratio	Tensile Shear Strength, psi at 77°F	at 500°F
67/33	2675	645
50/50	2315	1070
33/67	1900	1370
25/75	2000	1605
20/80	1715	1520
10/90	1390	1150
0/100	1240	1270

For adhesive bonds aged 200 hours at 500°F

EPON 864/Plyophen 5023 Resin Ratio	Tensile Shear Strength, psi at 77°F	at 500°F
67/33	465	370
50/50	420	205
33/67	295	215
25/75	280	205
20/80	200	160
10/90	0	0
0/100	50	0

The bend strength of EPON 864 - Plyophen 5023 adhesives decreased progressively from a value of 126 lbs to 83 lbs as the EPON 864 resin content was decreased from 67 to 10%.

Evaluation of Various Curing Agents

Dicyandiamide, the first curing agent used in the preparation of high temperature adhesives, has proved to be the most effective curing agent for combinations of EPON resins and Plyophen 5023. The compounds, evaluated in comparison with the performance of dicyandiamide in EPON 1001 - Plyophen 5023 adhesives, included the following: dimethylolurea, diallylmelamine, hexamethylenetetramine, toluene sulfonyl chloride, Catalyst C (Shell Chemical Company) and the ethyltriacetoxysilane complex of DMP-30. The adhesive formulations are described in Table 8 (50/50 EPON 1001/Plyophen 5023 resin ratio), in Table 9 (33/67 EPON 1001/Plyophen 5023 resin ratio) and in Table 10 (25/75 EPON 1001/Plyophen 5023 resin ratio). None of the curing agents appeared to be as effective as dicyandiamide for the production of high adhesive bond strength. In addition, no improvement in thermal resistance on long time aging was noted in the limited number of experiments. Illustrative test data for 33/67 EPON 1001/Plyophen 5023 adhesives (containing aluminum dust filler) which were cured for one-half hour at 330°F are given below:

Curing Agent, phr	Tensile Shear Strength, psi at 77°F	at 500°F
8 diallylmelamine	1365	800
1 Catalyst C	935	670
5 dicyandiamide	2000	1260

Several epoxide resin catalysts and cross-linking agents for epoxy and phenolic resins were also evaluated as co-reactants in EPON 1001 - Plyophen 5023 adhesives cured with dicyandiamide. The compounds included oxalic acid, sodium methoxide, sodium glycolate, dimethylolurea, urea, hexamethylenetetramine, paraformaldehyde, Melmac 401 (melamine-formaldehyde resin), diphenylsilanediol and ethyltriacetoxysilane. The formulations and test results for the EPON 1001-Plyophen 5023 adhesives are given in Table 8 (50/50 resin ratio), in Table 9 (33/67 resin ratio) and in Table 10 (25/75 resin ratio). No significant increase in adhesive bond strength or thermal stability was observed for systems cured with dicyandiamide and an additional cross-linking agent. Examples of aluminum dust filled adhesives from a blend of 50/50 EPON 1001/Plyophen 5023 and cured with dicyandiamide (5 phr) for one-half hour at 330°F are cited below:

Co-curing Agent, phr	Tensile Shear Strength at 500°F, psi Original	Aged 200 hrs at 500°F
2 dimethylolurea	1045	300
2 hexamethylenetetramine	385	
2 Melmac 401	870	0
2 urea	1205	0
2 diphenylsilanediol	980	335
None	1075	340

Dicyandiamide Concentration

The effect of dicyandiamide concentration upon adhesive bond strength was evaluated in 50/50 and 33/67 resin ratios of EPON 1001/Plyophen 5023. Adhesive bonds were prepared with aluminum dust filled hot melt adhesives in which the concentration of dicyandiamide was varied from 0 to 10 phr. The bonds were cured at contact pressure for one-half hour at 330°F. Shear strength tests were conducted at room temperature and at 500°F for five series of experiments. The evaluation was also extended to include the shear tests of samples aged for 200 hours at 500°F for one series of experiments. The experimental data are summarized in Table 11 (for the 50/50 resin ratio) and in Table 12 (for the 33/67 resin ratio).

In general, the experiments demonstrated that the dicyandiamide concentration is not critical in the range of 4 to 8 phr. Shear strength was *ca* 2000 psi at room temperature and *ca* 1400 psi at 500°F. Room temperature shear strength (1000 to 1500 psi) was lower, however, for bonds cured with 2 phr dicyandiamide or prepared without dicyandiamide. The curves plotted in Figure 6 give the average shear test results obtained for unaged

(Figure 6 follows)

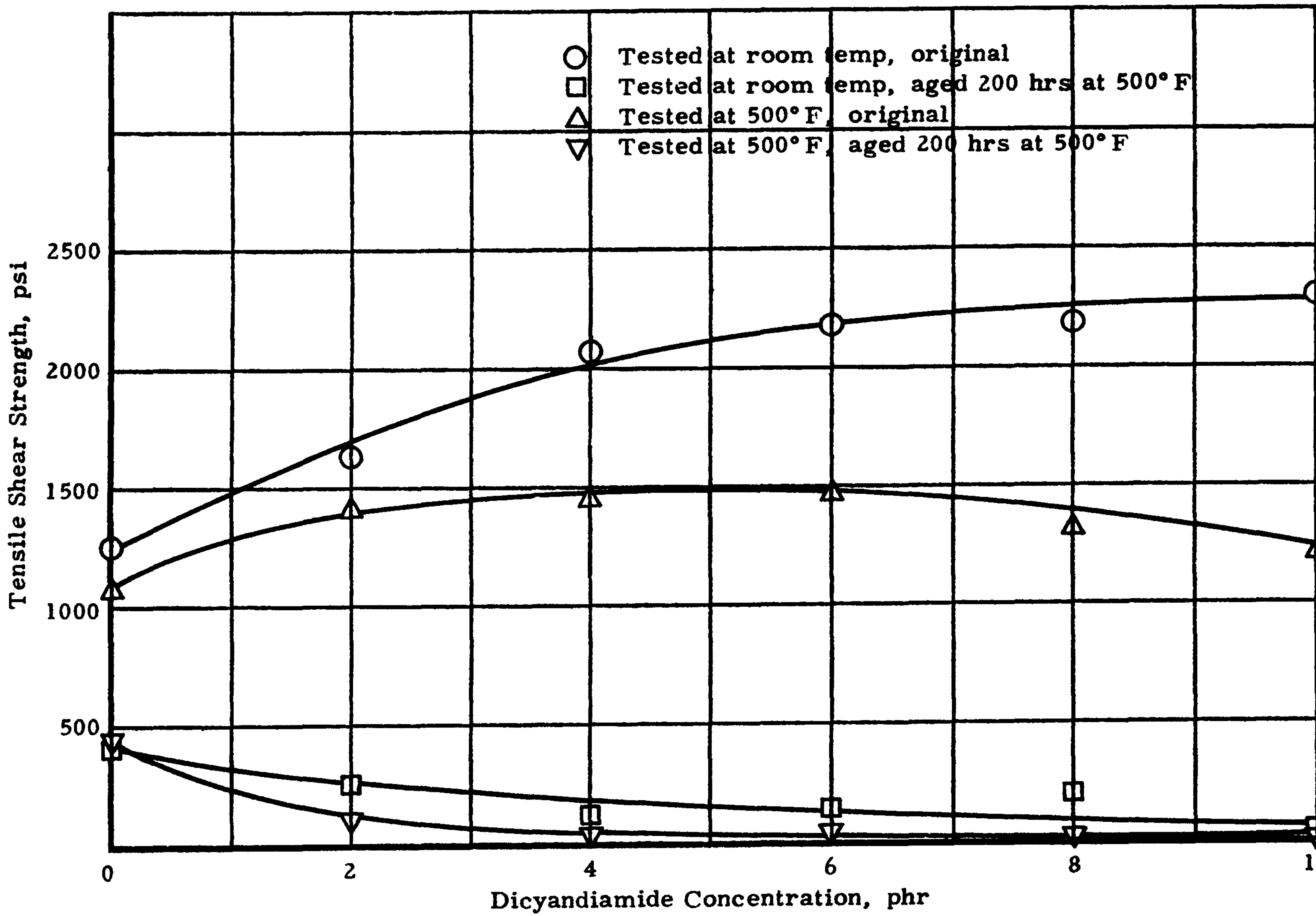

Figure 6. EFFECT OF DICYANDIAMIDE CONCENTRATION UPON THE TENSILE SHEAR STRENGTH OF 33/67 EPON 1001/PLYOPHEN 5023 ADHESIVES

Constant: 100 phr aluminum dust

Cure: one-half hour at 330° F

adhesive bonds in four series of experiments using a 33/67 EPON 1001/Plyophen 5023 resin ratio. These data are summarized below:

Dicyandiamide, phr	Tensile Shear Strength, psi at 77°F	at 500°F
0	1255	1080
2	1630	1405
4	2070	1430
6	2165	1450
8	2155	1300
10	2300	1200

Strength retention of aged (500°F) 33/67 EPON 1001/Plyophen 5023 adhesives with varying dicyandiamide content appeared to be maximum for adhesive bonds prepared without the curing agent. Shear strength was ca 400 psi after 200 hours at 500°F. The limited test data indicated that the strength of aged bonds decreased with increasing dicyandiamide concentrations. (See Figure 6).

Evaluation of Various Fillers

Aluminum dust (spherical particles, 84% finer than 325 mesh) was the first filler used in high temperature adhesive formulations from combinations of EPON resins and Plyophen 5023. Subsequent evaluation of a large number of materials showed that maximum bond strength and heat resistance was obtained with aluminum dust. In a comparison of the performance of aluminum dust, short and long fiber asbestos, powdered mica, Celite 270 and ferric oxide in a blend of 50/50 EPON 1001/Plyophen 5023, short fiber asbestos was the only material which looked promising (see Table 13). It was found, however, that asbestos filler was deleterious to the storage life of the adhesive.

A more extensive study of fillers was made for adhesive bonds from a blend of 33/67 EPON 1001/Plyophen 5023. The fillers included the following metals (zinc dust and pigment grade aluminum powder), colloidal silicas and fibrous silicates (Celite Filter-Aid, Hi-Sil, silica gel, ground fiber glass and Fiberfrax), clays and titanium dioxide. The adhesives were loaded with the maximum amount of filler which would permit good spreading of the hot melt. The adhesive bonds were cured with 5 to 6 phr dicyandiamide for one-half hour at 330°F. Shear strength tests were conducted at room temperature and at 500°F before and after aging for 200 hours at 500°F. The data are summarized in Table 14. None of the fillers appeared to be a better choice than aluminum dust in the development of high temperature strength and thermal resistance upon aging.

Aluminum Dust Concentration

The effect of aluminum dust concentration upon adhesive bond strength was evaluated in blends of 33/67 EPON 1001/Plyophen 5023 and EPON 864/Plyophen 5023. Hot melt adhesives were prepared with 0, 20, 60 and 100 phr aluminum

dust and cured with 5 to 6 phr dicyandiamide for one-half hour at 330°F. Shear strength tests were conducted at room temperature and at 500°F for unaged bonds and also for bonds aged 200 hours at 500°F. The effect of elevated temperature aging at 300°F and at 400°F was also determined for the EPON 864-Plyophen 5023 adhesives of varying aluminum dust content. The test results for the EPON 1001-Plyophen 5023 adhesives are given in Table 15; EPON 864-Plyophen 5023 adhesives are given in Table 16.

In general, the shear strength at room temperature and at 500°F increased progressively as the aluminum dust concentration was increased from 0 to 100 phr. The degree of strength retention upon 500°F aging, however, varied inversely as the aluminum dust content. Typical data are plotted in Figure 7 and are also summarized as follows:

For unaged adhesive bonds

Al dust, phr	Tensile Shear Strength, psi	
	at 77°F	at 500°F
0	910	660
20	1485	965
60	1995	1260
100	2160	1510

For adhesive bonds aged 200 hours at 500°F

Al Dust, phr	Shear Strength at 500°F, psi	Strength Retention, %
0	255	39
20	385	40
60	305	24
100	45	ca 10

Varying the aluminum dust filler loading in 33/67 EPON 864/Plyophen 5023 adhesives had the same effect upon adhesive strength as that observed for comparable EPON 1001 adhesives. The effect of filler content upon the shear strength of adhesive bonds aged for 200 hours at 300°F, 400°F and 500°F is shown in Figure 8.

Effect of Additives

In addition to the co-curing agents described in a previous section of this report, several other compounds were evaluated in EPON 1001-Plyophen 5023 adhesives with reference to the effect upon the thermal stability of the adhesive bonds. The compounds included AgeRite Alba and AgeRite Powder (antioxidants) cobalt naphthenate drier, and copper salicylaldoxime. Shear test results for bonds cured with 5 to 6 phr dicyandiamide for one-half hour at 330°F are summarized in Table 17. No appreciable change in adhesive shear strength was observed for unaged adhesive bonds prepared with the modified adhesives. One of the additives, copper salicylaldoxime, showed promise for

 (Figures 7 and 8 follow)

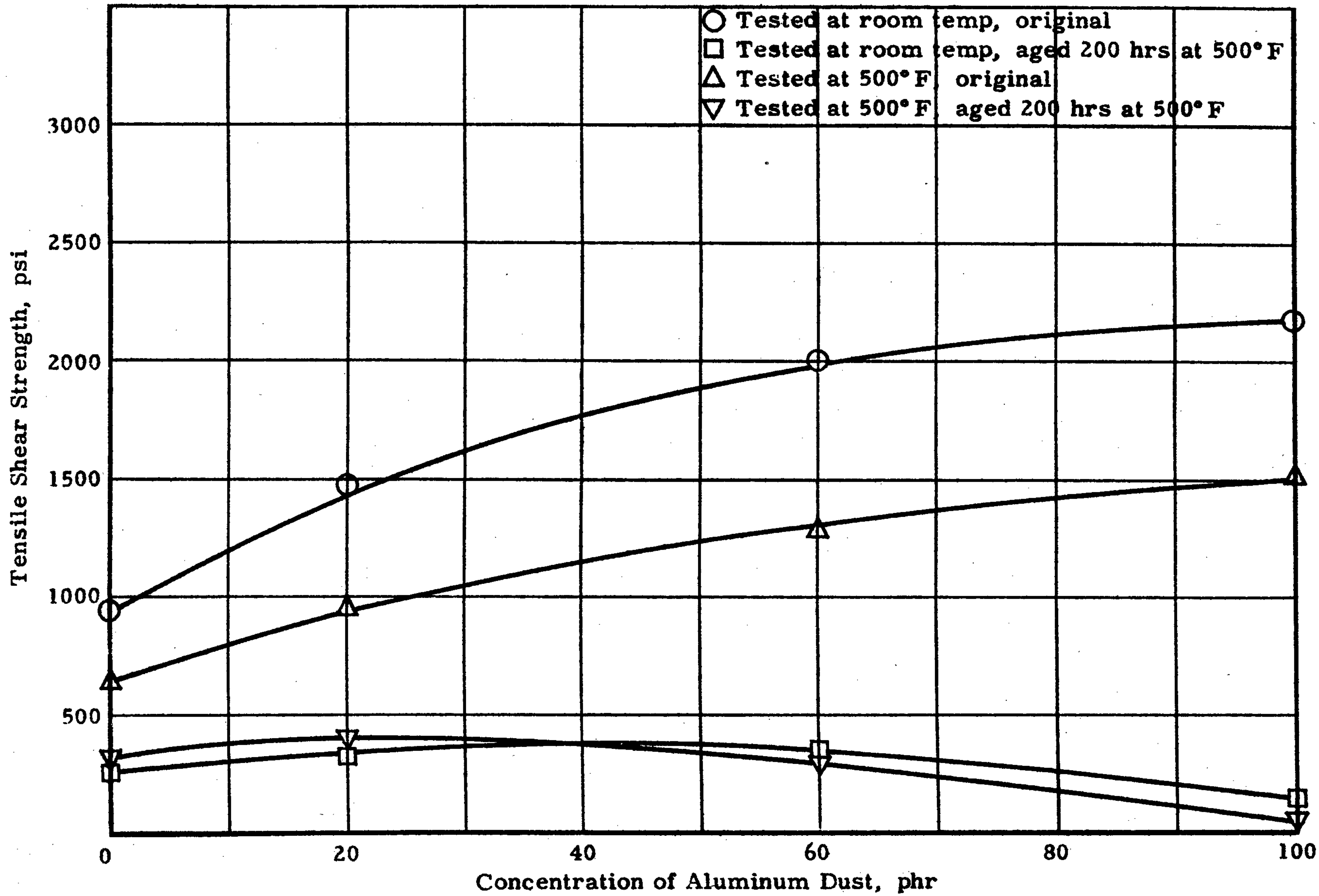

Figure 7. EFFECT OF ALUMINUM DUST FILLER UPON THE ADHESIVE BOND STRENGTH OF A 33/67 EPON 1001-PLYOPHEN 5023 ADHESIVE
Cure: 6 phr dicyandiamide for one-half hour at 330° F

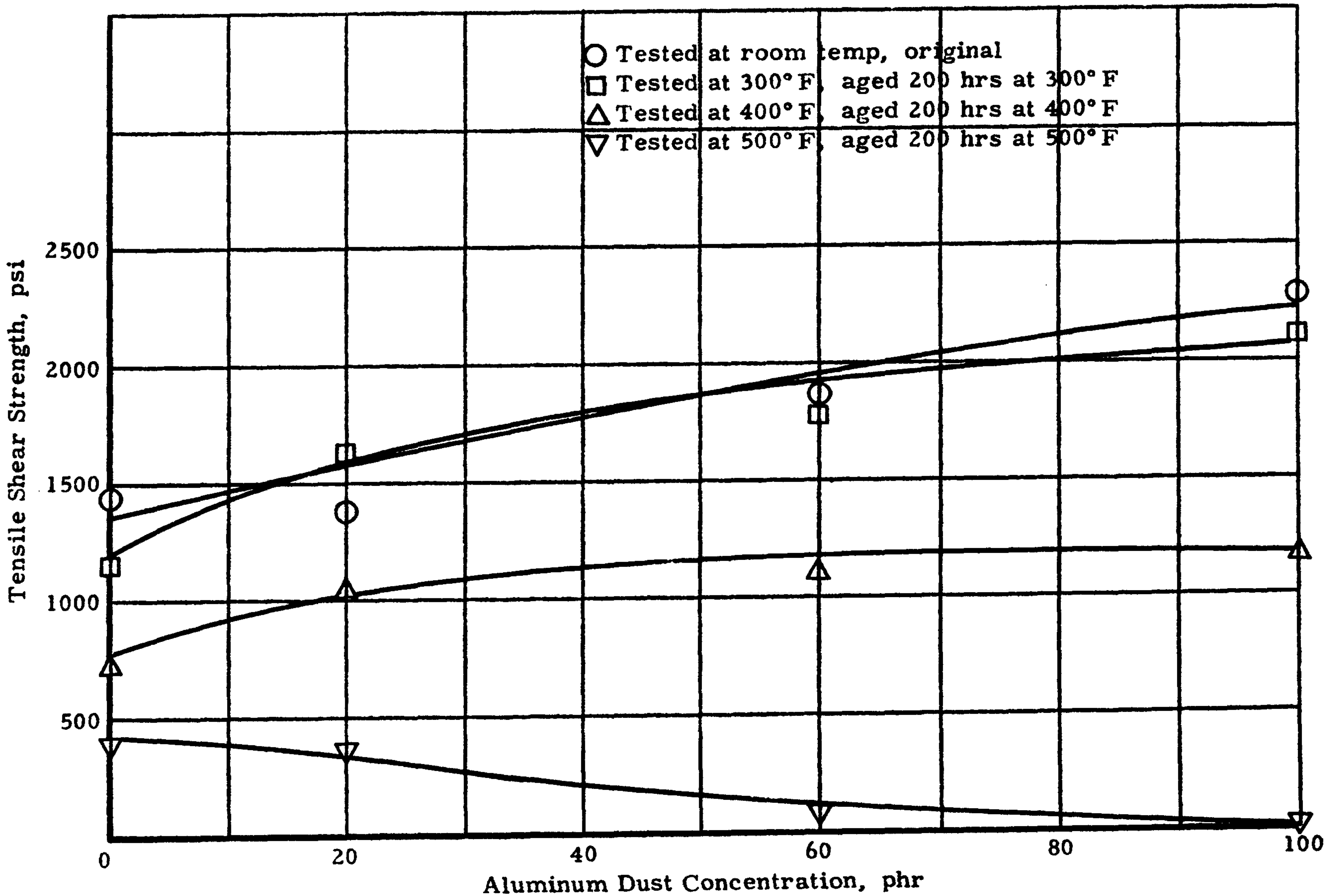

Figure 8. EFFECT OF ALUMINUM DUST CONCENTRATION UPON THE TENSILE SHEAR STRENGTH OF 33/67 EPON 864/PLYOPHEN 5023 ADHESIVES

Cure: 6 phr dicyandiamide for one-half hour at 330° F

the improvement of the thermal stability of adhesive Formulation No. 422 upon elevated temperature aging. The test results for the aged adhesive bonds follow:

Additive, phr	Tensile Shear Strength at 500°F after 200 Hours at 500°F, psi
0.5 copper salicylaldoxime	575
1.0 AgeRite Alba	55
1.0 AgeRite Powder	110
1.0 cobalt naphthenate drier	85
None	45

Effect of Precure

Adhesive bonds from Formulation No. 422 (and modifications) were usually cured for one-half hour at 330°F. Some experiments were conducted, however, to determine the effect of a precure at lower temperature for it had been observed that the adhesive glue lines were very porous. In addition, some improvement in reproducibility of bond strength performance was desired. Lower temperature precures were tried in order to induce gassing before the final cure and to promote interaction of the epoxy and phenolic resins. Adhesive formulations containing 6 phr dicyandiamide were precured in an oven at contact pressure for 30 to 60 minutes at 165°F to 200°F and then cured in the usual manner. Shear strength test results obtained at room temperature and at 500°F are summarized in Table 18.

The application of a precure at moderate temperatures reduced the porosity of the adhesive glue line and increased the adhesive shear strength approximately 10%. Experience with a large number of adhesive bonds has shown that the effectiveness of a precure is influenced by the temperature and heating period used for the preparation of the adhesive. Experiments to date indicate that a precure of 15 to 30 minutes at 165 to 200°F increases adhesive strength of bonds prepared from fresh adhesive. Typical data follow:

Precure		Shear Strength, psi	
min	°F	at 77°F	at 500°F
30	165	2620	1645
30	200	2200	1685
15	300	2255	1440
None		2170	1500

Effect of Solvents

Solution type adhesives based on EPON-1001/Plyophen 5023 adhesives were investigated because of the difficult handling properties of hot melt adhesives in shop practice and the poor storage life of adhesive tapes of 100% active ingredients. Several solvent systems for EPON 1001/Plyophen 5023 adhesives (50/50, 33/67 and 30/70 resin ratios) are summarized in Table 19.

The solvents included the following: methyl ethyl ketone-tetrahydrofurfuryl alcohol, methyl ethyl ketone-acetone-water, dimethylformamide-tetrahydrofuran, and dimethylformamide-methyl ethyl ketone-ethyl alcohol. Adhesive bond strength, especially at 500°F, was mediocre for each of the bonds prepared with the adhesive solutions. The methyl ethyl ketone-acetone-water solution of a 33/67 EPON 1001/Plyophen 5023 adhesive showed some promise, and further work appears justified. In general, shear strength at room temperature and at 500°F for bonds prepared with adhesive solutions was 60% and 33%, respectively, of the values obtained with hot melt adhesives.

Adhesives Based on Combinations of EPON Resins and Plyophen 5023

Combinations of various commercial and experimental EPON resins with Plyophen 5023 were evaluated as high temperature adhesives in the early phases of the research program. The EPON resins included the following: liquid resins, EPON 828 and EPON 834; solid resins of higher molecular weight than EPON 1001, EPON 1004 and EPON 1007; solid experimental resins EPON X-12100 and LR 564-46-59 which are more aromatic than the commercial EPON resins; EPON 864 and an experimental resin derived from EPON 864. Adhesive formulations based on blends of EPON resin X-12100 and Plyophen 5023 are summarized in Table 20. Adhesives derived from the other EPON resins and Plyophen 5023 are given in Table 21 (50/50 resin ratio), Table 22 (33/67 resin ratio) and in Table 23 (25/75 resin ratio).

Adhesive bonds prepared from a blend of EPON X-12100 and Plyophen 5023 were comparable to corresponding EPON 1001 adhesives in high temperature strength, but the glue lines were more brittle and also showed no appreciable improvement in thermal stability upon long time aging at elevated temperatures.

Adhesives based on the liquid EPON resins (EPON 828 and EPON 834) and Plyophen 5023 were superior to corresponding EPON 1001 adhesives in handling characteristics. Bond strength, particularly at 500°F, was mediocre; shear strength at 500°F was 550-780 psi, approximately one-half the value obtained for comparable EPON 1001 adhesives.

The performance of adhesive formulations based on combinations of EPON 864 or modified 864 and Plyophen 5023 was comparable to that of corresponding EPON 1001 adhesives. No appreciable improvement in storage life, handling characteristics, or thermal resistance was observed.

Poor bond strength was obtained in the evaluation of adhesives based on high molecular weight, high melting EPON resins (EPON 1004 and EPON 1007) and Plyophen 5023. The high melting point of the resin and the rapid reactivity with the phenolic resin precluded the preparation of a workable adhesive.

In general, EPON 1001-Plyophen 5023 adhesives (prepared from hot melt mixtures) were superior to combinations of Plyophen 5023 and the other types of commercial and experimental EPON resins.

Adhesives Based on Combinations of EPON Resins and Phenolic Resins (other than Plyophen 5023)

Several phenolic resins (other than Plyophen 5023) were evaluated as components of EPON high temperature adhesives. The resins chosen for the evaluation represented several different types of phenolics, namely, a liquid, one-stage laminating resin (Plyophen 5015), solid one-stage grindable rapid curing resins of high phenolic hydroxyl content (Resinox 618 and Resinox 665) and an alcohol soluble, high molecular weight phenol-formaldehyde novolac (Lebec 102594).

The adhesive formulations based on blends of Resinox 665 and EPON resins are summarized in Table 24. Adhesion to metal was poor for all formulations and despite the good thermal stability of Resinox 665, the adhesive shear strength at 500°F was very low, 100-500 psi.

The performance of Resinox 618-EPON resin adhesives was comparable to that of corresponding Resinox 665-EPON resin combinations (see Table 25).

Plyophen 5015 which is similar to Plyophen 5023 in methylol content was dehydrated to a water content of 3.5% from the original water content of ca 30%. The resin did not appear to afford any significant advantages over Plyophen 5023 in storage life or handling properties. In addition, no improvement in adhesive bond strength or thermal resistance was observed. The data are given in Table 25.

Very poor hot strength (25 to 190 psi at 500°F) was obtained in a limited number of evaluations of Lebec resin 102594 combined with EPON resins 1007 and X-12100. (Table 25)

Adhesives Based on Combinations of EPON 1001 and Silicone Resins

A brief study was made of adhesive formulations containing blends of EPON 1001 and various silicone resins. Dow-Corning resins XR-398, XR-261, and XR-384 were combined with EPON 1001 in solution systems; hexamethylenetetramine and DMP-30 were used as curing agents. No cure was obtained at a practical curing temperature of 330°F, even though the curing period was extended to 2 to 4 hours. Shear strength of adhesive bonds was very low at room temperature (160 to 1110 psi) and negligible at 500°F. The experiments are described in Table 26.

Adhesives Based on Experimental EPON Resins

The first program pursued in the development of high temperature adhesives was the evaluation of several experimental EPON resins in adhesive formulations. The experimental resins are characterized, in general, by a higher degree of aromaticity and by greater functionality compared with commercial EPON resins. It was expected that these properties would increase the heat resistance of the cured resin.

Dicyandiamide, one of the best curing agents for solid commercial EPON resins, was blended with the finely ground experimental epoxy resins. The resultant adhesive powders were applied to preheated (250°F) aluminum panels or to an undercoat of liquid EPON resin. The adhesive bonds were cured for one-half hour at 330°F. Adhesive strength data at room temperature and at elevated temperatures indicated that the heat resistance of the cured resins was inadequate for the development of an adhesive for 500°F service. (See Table 27). The 300°F shear strength of adhesive bonds from experimental EPON resin X-12100 was considerably greater than that obtained with commercial EPON resins; the 500°F shear strength was mediocre, however. The adhesive was also very brittle. Typical data for adhesive bonds cured with 5 phr dicyandiamide follow:

EPON Resin	Tensile Shear Strength, psi at 77°F	at 300°F	at 500°F
X-12100	2415	1400	385
864 (commercial grade)	4350	700	200
LR 564-46-59	4200		135

Procedure for Preparing Aluminum Surfaces for Bonding

Clad aluminum alloy 24S-T3 panels (thickness 0.064 in) were used in the evaluation of practically all adhesive formulations. A few bonds were also prepared with the unclad aluminum alloy. Each of these metals was prepared for bonding by the same procedure described below. (The panels were generally used within a month after preparation.)

1. Degreased with liquid trichloroethylene.
2. Rinsed with liquid trichloroethylene.
3. Vapor degreased with trichloroethylene for 30 seconds.
4. Etched with sulfuric acid-dichromic solution for 10 minutes at 160°F to 170°F. Composition of acid bath (by wt): one part sodium dichromate dihydrate + 5 parts concentrated sulfuric acid (sp. grav. 1.84) + 34 parts water.
5. Rinsed thoroughly in running water.
6. Dried for about five minutes at ca 200°F.

Table 1. ADHESIVE STRENGTH OF BONDS TO ALUMINUM FROM FORMULATION NO. 422

Adhesive formulation (parts by wt): 33 EPON 1001 + 67 Plyophen 5023 + 100 aluminum dust + 6 dicyandiamide
Cure: Oven heating at contact pressure for one-half hour at 330°F

Test [1]	Number of Adhesive Batches Tested	Number of Specimens Tested	Range	Average
Tensile shear strength, original values, psi				
At -70°F	3	9	1880-2650	2265
At room temperature	29	96	1540-2870	2110
At 300°F	4	12	1530-2410	1835
At 400°F	1	3	1430-2090	1755
At 500°F	29	93	1000-1710	1370
At 600°F [2]	1	2	1110-1175	1140
At 700°F [3]	2	2	830-915	870
Tensile shear strength, aged 200 hrs at 300°F, psi				
At room temperature	1	3	1520-2250	1875
At 300°F	1	3	2100-2540	2345
Tensile shear strength, aged 200 hrs at 400°F, psi				
At room temperature	1	3	1080-1440	1250
At 400°F	1	3	1260-1460	1340
Tensile shear strength, aged 200 hrs at 500°F, psi				
At -70°F	1	3	390-420	405
At room temperature	4	12	80-350	180
At 500°F	4	12	20-240	100
Tensile shear strength, weathered 2.5 months, [4] psi				
At room temperature	1	3	2180-2540	2370
At 500°F	1	3	1600-1630	1615
Tensile shear strength, weathered 6.5 months, [4] psi				
At room temperature	2	5	2000-2400	2190
At 500°F	1	2	1580-1750	1655
Bend strength at room temperature, [5] lbs	5	32	58-162	112
Long time load at 300°F, [6] 1200 psi	1	2	No failure at 144 hrs	
Long time load at 500°F, [2] 700 psi	1	1	No failure at 200 hrs	
Long time load at 500°F, [2] 1000 psi	1	1	Failure at 4.4 hrs	

1) Tests conducted on standard clad 24S-T3 aluminum alloy test strips with one-half inch lap joints according to U.S.A.F. specification 14164.
2) Data by Materials Laboratory, WADC.
3) Data by Materials Laboratory, WADC. Adhesive bond with glass fabric (grade 106) in the glue line: 990 psi (single determination).
4) Weathered at Emeryville, Calif. after 2 months' storage in the laboratory.
5) Bend strength with glass fabric (grade 667) in the glue line: 138 lbs (average of three tests).
6) Static shear test at 300°F after long time loading: 2400 psi (one test specimen).

Table 2. TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM FORMULATION NO. 422 AFTER CYCLING AT ELEVATED TEMPERATURES

Adhesive tape batch number 22; cured for one-half hour at 330°F at contact pressure.[1)]

Number of Cycles	Cycled at 300°F[2)]				Cycled at 400°F[2)]				Cycled at 500°F[2)]			
	Test at 77°F, psi		Test at 300°F, psi		Test at 77°F, psi		Test at 400°F, psi		Test at 77°F, psi		Test at 500°F, psi	
	Range	Avg.[3)]	Range	Avg.[3)]	Range	Avg.[3)]	Range	Avg.[3)]	Range	Avg.[3)]	Range	Avg.[3)]
0	2380-2870	2685	2290-2410	2335	2380-2870	2685	1430-2090	1755	2380-2875	2685	1100-1580	1345
5	2030-2800	2530	2120-2220	2175	1890-2000	1950	1800-1890	1865	1000-1400	1245	1220-1410	1345
15	--	--	2230-2430	2350	--	--	1800-2000	1885	--	--	950-1370	1225
25	--	--	2080-2230	2200	--	--	1870-1980	1915	--	--	1020-1340	1200
40	--	--	2110-2180	2150	--	--	1970-2090	2035	--	--	1280-1320	1295
50	1950-2240	2065	2060-2390	2180	1800-2220	2070	1940-2060	2000	890-1160	1055	1220-1290	1255

1) Formulation (parts by wt): 33 EPON 1001 + 67 Plyophen 5023 (lot no. SWL-523) + 100 aluminum dust + 6 dicyandiamide.

2) Bonded test specimens on standard clad 24S-T3 aluminum alloy were heated in an oven for 30 minutes and then allowed to cool to room temperature. The procedure was repeated for the prescribed number of cycles and then tested at the preheating temperature.

3) Average of three values. All breaks were cohesive type failures.

Table 3. EFFECT OF FLUID EXPOSURE UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM FORMULATION NO. 422

Adhesive formulation (parts by wt): 33 EPON 1001 + 67 Plyophen 5023 + 100 aluminum dust + 6 dicyandiamide

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Tensile Shear Strength at Room Temperature,[1] psi	Number of Batches Tested	Number of Specimens Tested	Range	Average
Original	6	18	1540-2550	2100
After 30 days salt spray exposure	4	24	1600-2470	2180
After 30 days immersion in tap water	5	29	1420-2530	2050
After 8 days immersion in ethylene glycol	2	12	1500-2460	1980
After 8 days immersion in anti-icing fluid	2	12	1850-2440	2160
After 8 days immersion in hydraulic oil	2	12	1410-2220	2010
After 8 days immersion in hydrocarbon fluid	3	18	1750-2440	2030

1) Tests conducted according to U.S.A.F. specification 14164.

Table 4. TENSILE SHEAR STRENGTH OF 33/67 EPON 1001/PLYOPHEN 5023 ADHESIVE BONDS TO 301 STAINLESS STEEL

Bonds to 301 stainless steel (17/7) with full hard temper and 2B finish; thickness 0.050 in.

Sample No.[1]	Plyophen 5023 Lot No.	Dicy,[2] phr	Surface Treatment[3]	Shear Strength,[4] psi at -70°F	at 77°F	at 500°F
445J-10A	AZA-289	5	None		1985	1640
445J-10B	"	"	Sandblast		2275	1585
445J-8C	"	"	Conc. hydrochloric acid[5]		2905	1600
445J-8D	"	"	Hydrofluoric acid-nitric acid[6]		1835	1575
445J-8E	"	"	Wash primer WP-1[7]		1785	165
422J-27B[8]	SWL-523	6	Sandblast	1730	1905	1250
422J-27C[8]	"	"	Conc. hydrochloric acid[5]	2025	2725	1280

1) Adhesive tape formulation (parts by wt.): 33 EPON 1001 + 67 Plyophen 5023 + 100 aluminum dust. Cure: oven heating at contact pressure for one-half hour at 330°F.

2) "Dicy" is dicyandiamide.

3) Before surface treatment the metal was degreased with trichloroethylene and with an alkaline detergent solution (3 oz. sodium metasilicate, 1.5 oz. tetrasodium pyrophosphate, 1.5 oz. sodium hydroxide, 0.5 oz. Nacconal NR in one gallon water).

4) Average of three values for bonds with one-half inch lap joints (1.0 in. x 0.050 in. x 7.5 in.).

5) Etched with concentrated hydrochloric acid (37% by weight) for 10 min. at room temperature; rinsed and then dried at ca 200°F.

6) Etched with dilute sulfuric acid (10% by volume) for 15 min. at 140°F; rinsed and given a "bright dip" in hydrofluoric acid (2% by volume) - nitric acid (15% by volume) solution for 10 min. at 120°F; rinsed and then dried at ca 200°F.

7) Bakelite wash primer WP-1 (polyvinyl butyral - zinc chromate - phosphoric acid coating).

8) Bonds broke on handling after oven aging for 200 hours at 500°F.

Table 5. EFFECT OF EPON 1001/PLYOPHEN 5023 RESIN RATIO UPON ADHESIVE STRENGTH USING 60 PHR ALUMINUM DUST FILLER

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No.[1]	EPON 1001/ Plyophen 5023 Resin Ratio	Dicy,[2] phr	Tensile Shear Strength,[3] psi			
			Original		Aged 200 hrs. at 500°F	
			at 77°F	at 500°F	at 77°F	at 500°F
372J[4]	50/50	4	2510	925	725	510
372J-1[5]	"	4	1945	1240	330	305
405M[6]	"	4	2755	955		405
397J-6	"	5	2640	950		340
395J	33/67	4	2000	1345	560	505
373J[7]	25/75	4	1680	1550		
373P[8]	25/75	4	1970	1375	205	0

1) Constant ingredient of hot melt adhesives formulated with Plyophen 5023 (lot no. SWH-742): 60 phr aluminum dust.

2) "Dicy" is dicyandiamide.

3) Average of three values for standard test joints on unclad 24S-T3 aluminum alloy.

4) Shear strength at 300°F: 1605 psi; shear strength at 400°F: 1515 psi.

5) Bonds on clad 24S-T3 aluminum.

6) Adhesive stick prepared from the chilled adhesive mix. The stick was preheated for 10 min. at 200°F and 20 min. at 125°F before application to the metal.

7) Shear strength at 300°F: 1645 psi.

8) Adhesive bond precured one-half hour at 290°F.

Table 6. EFFECT OF EPON 1001/PLYOPHEN 5023 RESIN RATIO UPON ADHESIVE STRENGTH USING 100 PHR ALUMINUM DUST FILLER

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No. 1)	EPON 1001/ Plyophen 5023 Resin Ratio	Plyophen 5023 Lot No.	Dicy, 2) phr.	Precure		Tensile Shear Strength, 3) psi				Bend Test at 77°F, lbs.
				Min	°F	Original		Aged 200 hrs. at 500°F		
						At 77°F	at 500°F	at 77°F	at 500°F	
491V	67/33	AZA-289	5	30	200	2700	475	465	315	
491J-2	"	SWL-523	"	-	-	2585	590	465	465	148
492V	50/50	AZA-289	5	30	200	2430	1170	275	125	
492J-2	"	SWL-523	"	-	-	2265	1065	345	305	116
413M 4)	"	SWH-742	4	(5)	200	3160	1415	655	445	
394J	33/67	"	4	-	-	2275	1325	520	385	
422J-3	"	"	6	-	-	2120	1520	305	215	
445V-1	"	AZA-289	5	30	200	1775	1375	255	0	
445J-27	"	SWL-523	"	-	-	1755 6)	1380	300	375	
461W	30/70	SWH-742	"	60	200	2130	1765	265	115	
493V	25/75	AZA-289	"	30	200	1665	1315	225	0	
493J-2	"	SWL-523	"	-	-	2040	1805	55	50	105
460V	20/80	AZA-289	"	30	200	1430	1385	235	0	
460J-2	"	SWL-523	"	-	-	1640	1705	50	50	87
460W	"	SWH-742	"	60	200	1435	1375			98
459W	10/90	"	"	60	200	1480	1255			81
583J	"	SWL-523	"	-	-	1675	1510	0	0	101
582J	0/100	"	"	-	-	1240	1270	25	0	84
458W	"	SWH-742	"	60	200	1330	715			71

1) Constant ingredient of hot melt adhesives: 100 phr aluminum dust.
2) "Dicy" is dicyandiamide.
3) Average of three values for standard, clad 24S-T3 aluminum alloy test strips.
4) An adhesive stick was cast after heating the adhesive for 15 min. at 200°F.
5) Panel pressed for 30 seconds at 50 psi and 200°F before curing.
6) This value is considerably lower than the average value of ca 2100 psi obtained for six previous preparations of this formulation.

Table 7. EFFECT OF EPON 864/PLYOPHEN 5023 RESIN RATIO UPON ADHESIVE BOND STRENGTH

Cure: Oven heating at contact pressure for one-half hour at 330°F

Formulation No.1)	EPON 864/ Plyophen 5023 Resin Ratio	Plyophen 5023 Lot No.	Precure		Tensile Shear Strength,2) psi				Bend Test at
					Original		Aged 200 hrs at 500°F		
			min	°F	at 77°F	at 500°F	at 77°F	at 500°F	77°F, lbs
494V-1	67/33	AZA-289	30	200	3085	645	615	350	
494V-2	67/33	AZA-289	30	200	3075	585			
494J-3	67/33	SWL-523	--	---	2740	645	465	370	126
496V	50/50	AZA-289	30	200	2740	1265			156
496J-1	50/50	SWL-523	--	---	2315	1070	425	305	125
392J3)	50/50	SWH-742	--	---	2575 4)	825 4)	765 4)	580 4)	
392J-1 3)	50/50	SWH-742	--	---	2205	1040	285	105	
495V-1	33/67	AZA-289	30	200	2070	1485	305	105	
495J-3	33/67	SWL-523	--	---	1900	1370	295	215	116
487V3)	33/67	SWL-523	30	200	1615	1325			
497V	25/75	AZA-289	30	200	1380	820			106
497J-1	25/75	SWL-523	--	---	2000	1605	280	205	119
498J	20/80	SWL-523	--	---	1655	1345			100
498J-1	20/80	SWL-523			1715	1520	195	160	110
581J	10/90	SWL-523	--	---					
					1390	1150	0	0	83
582J	0/100	SWL-523	--	---	1240	1270	15	0	84

1) Constant ingredients of hot melt adhesives: 100 phr aluminum dust + 5 phr dicyandiamide.
2) Average of three values for standard clad aluminum alloy (24S-T3) test strips.
3) Formulation contained 60 phr aluminum dust.
4) Bonds to unclad 24S-T3 aluminum.

Table 8. EFFECT OF CURING AGENTS UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM A BLEND OF 50/50 EPON 1001/PLYOPHEN 5023

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No.[1]	Dicy,[2] phr	Co-curing Agent, phr	Tensile Shear Strength, psi			
			Original		Aged 200 hrs at 500°F	
			at 77°F	at 500°F	at 77°F	at 500°F
390J[4]	None	8 dimethylolurea	850	965		
408J	5	2 dimethylolurea	2345	1045	465	300
409J	5	2 hexamethylenetetramine	2935	385		
410J	5	2 Melmac 401	2810	870	520	0
407J	5	2 urea	2420	1205	205	0
411J	5	2 diphenylsilanediol	2305	1060		
411J[5]	5	2 diphenylsilanediol	1830	980	390	335
411K[6]	5	2 diphenylsilanediol	2500	780		
472J[7]	None	10 DMP-30-ethyltriacetoxysilane	945	150		
397J	5	None	2855	1075	775	340
392J	4	None	2575	825	765	580
392J-1[5]	4	None	2205	1040	285	205

1) Constant ingredient of hot melt adhesives: 60 phr aluminum dust filler.
2) "Dicy" is dicyandiamide.
3) Average of three values for standard unclad 24S-T3 aluminum alloy test strips.
4) Formulation contained no filler.
5) Clad aluminum alloy bonds.
6) Cure: one hour at 330°F.
7) Formulation contained 100 phr aluminum dust; clad aluminum alloy bonds.

Table 9. EFFECT OF CURING AGENTS UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM A BLEND OF 33/67 EPON 1001/PLYOPHEN 5023

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No.[1]	Dicy,[2] phr	Co-curing agent, phr	Precure		Tensile Shear Strength,[3] psi			
					Original		Aged 200 hrs at 500°F	
			min	°F	at 77°F	at 500°F	at 77°F	at 500°F
471J	4	10 oxalic acid[4]			510	630		
426J	5	1 sodium glycolate			1795	1305	185	125
431J	5	2 sodium glycolate			1695	1230		
395J[5]	4	None			2000	1355	560	505
469W[6]	6	1 sodium methoxide	60	200	1955	175	140	0
428J-3[6]	6	None			1895	1320	460	360
429J	4	8 dimethylolurea			1665	1445		
430J	4	12 dimethylolurea			1530	1255		
483V	5	4 diphenylsilanediol	30	200	1420	1390	240	0
484V	5	6 diphenylsilanediol	30	200	1260	1065		
485V	5	8 diphenylsilanediol	30	200	1485	1325		
486V	5	10 diphenylsilanediol	30	200	1535	1115	115	0
416J	5	None			2000	1260	325	305
456Q	None	8 diallylmelamine	30	165	1365	800		
422Q[7]	6	None	30	165	2620	1645		
509J[7]	None	1.0 Catalyst C			935	670	360	325
510J[7]	None	0.5 Catalyst C			1125	670		

1) Constant ingredient of hot melt adhesives: 60 phr aluminum dust.
2) "Dicy" is dicyandiamide.
3) Average of three values for standard clad 24S-T3 aluminum alloy test strips.
4) The phenolic resin was partially polymerized with oxalic acid and the resultant solid product mixed with the other solid ingredients. The adhesive powder was applied to an undercoat of liquid Plyophen 5023.
5) Test strips prepared from unclad 24S-T3 aluminum alloy.
6) Formulation contained 30 phr asbestos in place of aluminum dust filler.
7) Formulation contained 100 phr aluminum dust.

Table 10. EFFECT OF CURING AGENTS UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM A BLEND OF 25/75 EPON 1001/PLYOPHEN 5023

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No.[1]	Dicy,[2] phr	Co-curing Agent, phr	Tensile Shear Strength,[3] psi			
			at 77°F	at 300°F	at 400°F	at 500°F
373J	4	None	1680	1645		1550
373P[4]	4	None	1970			1375
383J	4	2 paraformaldehyde	1500	1435	1585	1665
384J[5]	None	7.5 hexamethylenetetramine	1215	1955	1615	1275
385J	None	7.5 hexamethylenetetramine	1825	2645	1375	1070
386J	None	10 toluene sulfonyl chloride	615	345		
425J[6]	5	3 ethyltriacetoxysilane[7]	1155			705

1) Constant ingredient of hot melt adhesives: 60 phr aluminum dust filler.

2) "Dicy" is dicyandiamide.

3) Average of three values for standard unclad 24S-T3 aluminum alloy test strips.

4) Bond precured for one-half hour at 290°F. Shear strength at room temperature after 200 hours at 500°F: 205 psi.

5) Formulation contained no filler.

6) Bond on clad aluminum alloy. Shear strength at room temperature after 200 hours at 500°F: 165 psi.

7) Plyophen 5023 treated with ethyltriacetoxysilane for 48 hours at room temperature and then mixed with the other adhesive ingredients.

Table 11. EFFECT OF DICYANDIAMIDE CONCENTRATION UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM A BLEND OF 50/50 EPON 1001/PLYOPHEN 5023

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No. 1)	Dicy,2) phr	Tensile Shear Strength,3) psi	
		at 77°F	at 500°F
372F	4	2510	925
397J	5	2855	1175
398J	6	2745	1025
399J	8	2665	1160
400J	10	2520	900

1) Constant ingredient of hot melt adhesives using Plyophen 5023 (lot no. SWH-742): 60 phr aluminum dust.

2) "Dicy" is dicyandiamide.

3) Average of three values for unclad 24S-T3 aluminum alloy test strips (1.0 in. x 0.064 in. x 8.5 in.).

Table 12. EFFECT OF DICYANDIAMIDE CONCENTRATION UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM A BLEND OF 33/67 EPON 1001/PLYOPHEN 5023

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No. 1)	Plyophen 5023 Lot No.	Dicy, 2) phr	Tensile Shear Strength, 3) psi			
			Original		Aged 200 hrs at 500°F	
			at 77°F	at 500°F	at 77°F	at 500°F
441J	SWH-742	0	1360	1150	395	310
442J	"	2	1675	1375		
443J	"	3	1805	1345		
444J	"	4	2175	1550		
445J	"	5	2005	1560		
422J-14	"	6	2270	1495		
446J	"	8	2290	1320		
442J-1	AZA-289	2	1665	1415		
444J-1	"	4	2375	1595		
422J-19	"	6	2365	1555		
446J-1	"	8	2515	1360		
539J-1	"	10	2550	930		
441J-2	SWL-523	0	1235	1115	400	435
442J-2	"	2	1635	1460	255	105
444J-2	"	4	1745	1295	105	45
422J-20	"	6	2160	1515	135	45
446J-2	"	8	1845	1370	195	25
539J-2	"	10	2225	1565	35 4)	0
442J-3	AZA-380	2	1535	1380		
444J-3	"	4	1975	1275		
422J-21	"	6	1860	1240		
446J-3	"	8	1975	1155		
539J-3	"	10	2130	1105		

1) Constant ingredient of hot melt adhesives: 100 phr aluminum dust.

2) "Dicy" is dicyandiamide.

3) Average of three values for standard clad 24S-T3 aluminum alloy test strips

4) Average of two values; one specimen broke on handling.

Table 13. EFFECT OF FILLERS UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM A BLEND OF 50/50 EPON 1001/PLYOPHEN 5023

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No.[1]	Filler, phr	Tensile Shear Strength,[2] psi			
		at 77°F	at 300°F	at 400°F	at 500°F
372J [3]	60 aluminum dust	2345	1605	1515	1345
378J	30 asbestos 7TF2	2570	1200		1120
382J	30 asbestos 7RF6	2575	1005	935	1085
308J	30 powdered mica	1025			400
381J	30 Celite 270	1850	670	515	500
396J [4]	60 ferric oxide	1825			470

1) Constant ingredient of hot melt adhesives: 4 phr dicyandiamide.

2) Average of three values for 24S-T3 (unclad) aluminum alloy test strips (1.0 in. x 0.0064 in. x 8.5 in.) with one-half inch lap joints.

3) Shear strength after 200 hours at 500°F: 725 psi at room temperature and 510 psi at 500°F.

4) Shear strength after 200 hours at 500°F: 300 psi at 500°F.

Table 14. EFFECT OF FILLERS UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM A BLEND OF 33/67 EPON 1001/PLYOPHEN 5023

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No. [1]	Filler, [2] phr	Tensile Shear Strength,[3] psi			
		Original		Aged 200 hrs at 500°F	
		at 77°F	at 500°F	at 77°F	at 500°F
422J-3	100 aluminum dust	2120	1520	305	215
422J-8	" " "	2175	1385		
422J-12	" " "	2520	1295		
422J-20	" " "	2160	1510	135	45
448J	30 aluminum powder	1280	545	450	390
499J	100 zinc dust	1820	1215	200	160
428J-1	30 asbestos 7TF2	1900	1400		
428J-3	" " "	1885	1320	460	360
447J	20 silica gel (< 100 mesh)	900	810	0	0
584J	" " " (< 325 mesh)	1400	1150	185	105
585J	40 " " (< 325 mesh)	1505	1055	180	110
555J	15 Celite, Filter-Aid	1600	1105	125	80
556J	25 " " "	1680	870	125	0
557J	15 Hi-Sil	1200	630	260	245
558J	30 Bentone 34	875	370	335	265
387J	70 Monetta clay	1540	645	500	245
588J	100 pyrophyllite clay	1595	910	430	275
541J	10 ground fiber glass	1155	1085		
559J	" " "	1405	1215	175	0
542J	5 " " "	1255	1035		
568J	{5 ground fiber glass {5 copper powder	1185	1165	320	205
543J	10 Fiberfrax	750	560		
590J	100 Titanox RA	1900	1095	370	280

1) Constant ingredient of hot melt adhesives: 6 phr dicyandiamide.

2) The filler was used at the maximum concentration permissible to insure good spreading of the hot melt adhesive.

3) Average of three values for standard clad 24S-T3 aluminum alloy test strips.

Table 15. EFFECT OF ALUMINUM DUST CONCENTRATION UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM A BLEND OF 33/67 EPON 1001/PLYOPHEN 5023

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No.[1]	Plyophen 5023 Lot No.	Dicy,[2] phr	Aluminum Dust, phr	Tensile Shear Strength,[3] psi			
				Original		Aged 200 hrs at 500°F	
				at 77°F	at 500°F	at 77°F	at 500°F
416V	AZA-289	5	60	1685	1265		
488V	AZA-289	5	70	1720	1315		
489V	AZA-289	5	80	1665	1140		
490V	AZA-289	5	90	1915	1205		
445V-1	AZA-289	5	100	1775	1375	255	0
575J	SWL-523	6	None	910	660	245	255
575J-2	SWL-523	6	None	1285	765	235	220
574J	SWL-523	6	20	1485	965	310	385
416J	SWL-523	6	60	1995	1260	325	305
422J-20	SWL-523	6	100	2160	1515	135	45

1) Adhesive formulations coded with a "V" were precured for one-half hour at 200°F.

2) "Dicy" is dicyandiamide.

3) Average of three values for standard clad 24S-T3 aluminum alloy test strips.

Table 16. EFFECT OF ALUMINUM DUST CONCENTRATION UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM A BLEND OF 33/67 EPON 864/PLYOPHEN 5023

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formula-No.[1]	Aluminum Dust, phr	Tensile Shear Strength,[2] psi							
		Original		Aged 200 hrs at 300°F		Aged 200 hrs at 400°F		Aged 200 hrs at 500°F	
		at 77°F	at 500°F	at 77°F	at 300°F	at 77°F	at 400°F	at 77°F	at 500°F
545J	None	1435	825					665	385
545J-2	None			1295	1115	780	695		
546J	20	1375	885					355	355
546J-2	20			1435	1640	1045	1045		
547J	60	1870	1085					225	75
547J-2	60			1625	1785	1035	1100		
548J	100	2295	1560					210	0
548J-2	100			1690	2105	865	1160		

1) Constant ingredient of hot melt adhesives using Plyophen 5023 (lot no. SWL-523): 6 phr dicyandiamide.
2) Average of three values for standard clad 24S-T3 aluminum alloy test strips.

Table 17. EFFECT OF VARIOUS ADDITIVES UPON THE ADHESIVE SHEAR STRENGTH OF BONDS FROM A BLEND OF 33/67 EPON 1001/PLYOPHEN 5023

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No.[1]	Additive, phr	Dicy,[2] phr	Tensile Shear Strength,[3] psi			
			Original		Aged 200 hrs at 500°F	
			at 77°F	at 500°F	at 77°F	at 500°F
514J	1.0 AgeRite Alba	5	1820	1200	200	55
515J	1.0 AgeRite Powder	5	1895	1225	210	110
516J	1.0 cobalt naphthenate drier[4]	5	1935	1310	205	85
445J-18	None	5	2000	1395	20	0
580J	0.5 copper salicylaldoxime	6	1870	1515	500	575
442J-20	None	6	2160	1515	135	45

1) Constant ingredient of hot melt adhesives: 100 phr aluminum dust.

2) "Dicy" is dicyandiamide.

3) Average of three values for standard clad 24S-T3 aluminum alloy test strips.

4) Solution contained 6% cobalt.

Table 18. EFFECT OF PRECURE UPON THE TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM FORMULATION NO. 422

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Panel No.	Adhesive Batch No.[1]	Precure[2]		Tensile Shear Strength at 77°F, psi		Tensile Shear Strength at 500°F, psi	
		min	°F	Range	Avg[3]	Range	Avg[3]
422J-14	14	None		2050-2390	2270	1400-1550	1500
422Q	14	30	165	2490-2720	2620	1610-1700	1645
422R[4]	14	60	300	2210-2490	2315	1370-1520	1455
422RT	14	(5)	75	2520-2650	2590	1240-1510	1350
422S	14	15	200	2370-2480	2445	1390-1770	1565
422T	14	15	250	2130-2160	2135	1230-1400	1305
422U	14	15	300	2190-2380	2255	1400-1470	1440
422W	14	60	200	1650-2310	2010	1600-2010	1800
422J-18	18	None		1990-2180	2070	1530-1680	1600
422Pr-18[6]	18	(7)		1500-1870	1715	1340-1520	1455
422V-18	18	30	200	2120-2370	2200	1580-1900	1685
422W-18	18	60	200	1580-2240	1845	1400-1640	1540

1) Adhesive tape composition (parts by wt): 33 EPON 1001 + 67 Plyophen 5023 (lot no. SWH-742) + 100 aluminum dust + 6 dicyandiamide.
2) Adhesive bonds heated at contact pressure in an oven.
3) Average of three values for standard clad 24S-T3 aluminum alloy test strips.
4) Cure: one hour at 330°F.
5) Adhesive bond allowed to stand at room temperature for 24 hours at contact pressure.
6) Cured in a press at 25 psi.
7) The panel was placed in a cold press and brought to the cure temperature (330°F) in 10 min.

Table 19. TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM SOLUTION TYPE ADHESIVES BASED ON EPON 1001 RESIN AND PLYOPHEN 5023

Formulation No.	EPON 1001/Plyophen 5023 Resin Ratio	Solvents,[2] phr	Curing Agent, phr	Filler, phr	Air Dry,[3] hrs.	Precure[3] at 200°F, min	Tensile Shear Strength,[4] psi	
							at 77°F	at 500°F
388L[5]	50/50	50 MEK + 36 THFA	4 dicy[6]	None	16	10	1405	445
402N[7]	"	50 MEK + 36 THFA	" "	100 ferric oxide	"	"	--	--
403N[7]	"	50 MEK + 36 THFA	" "	100 cement	"	"	--	--
404N[7]	"	50 MEK + 36 THFA	" "	100 aluminum powder	"	"	--	--
372J	"	None	" "	60 aluminum dust	None	None	2510	925
420J	"	50 MEK	7.5 hexa[8]	None	5	None	1505	350
384J	"	None	" "	None	None	None	1215	1275
454J	33/67	18 MEK + 24 acetone + 12 water	6 dicy	None	1	20	1675	780
575J	"	None	" "	None	--	--	975	660
474W-3[9]	30/70	18 DMF + 70 THF	5 dicy	None	16	10	1280	530
474W-7[9]	"	18 DMF + 70 THF	" "	None	3	20	1610	545
475W-4[9]	"	15 DMF + 40 MEK + 17.5 ETOH	" "	None	4	20	1345	535
475W-24[9]	"	15 DMF + 40 MEK + 17.5 ETOH	" "	None	24	20	1435	425
461W[9]	"	None	" "	100 aluminum dust	--	--	2130	1765

1) Cure: oven heating at contact pressure for one-half hour at 330°F.
2) MEK = methyl ethyl ketone; THFA = tetrahydrofurfuryl alcohol; DMF = dimethylformamide; THF = tetrahydrofuran; EtOH = ethyl alcohol.
3) Treatment of panels before assembly.
4) Average of three values for standard clad 24S-T3 aluminum alloy test strips.
5) Cure: one-half hour at 320°F at 50 psi. Bonds to unclad 24S-T3 aluminum.
6) "Dicy" is dicyandiamide.
7) Unclad 24S-T3 aluminum bonded panels broke on handling; cured at 50 psi.
8) "Hexa" is hexamethylenetetramine.
9) Assembled panels precured for one hour at 200°F.

Table 20. TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM COMBINATIONS OF EXPERIMENTAL EPON RESIN X-12100 AND PLYOPHEN 5023

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No.	Aluminum Metal, 24S-T3	EPON X-12100/ Plyophen 5023 Resin Ratio	Aluminum Filler, phr[1]	Dicy,[2] phr	Tensile Shear Strength,[3] psi			
					Original		Aged 200 hrs at 500°F	
					at 77°F	at 500°F	at 77°F	at 500°F
342J	Unclad	75/25	-	3.8	1745	360		
367J	Unclad	75/25	60 powder	4.0	1380	380		
341J	Unclad	67/33	-	3.3	1205	400		
366J	Unclad	67/33	60 powder	4.0	1285	560		
338J	Unclad	50/50	-	2.5	1530	520		
364J	Unclad	50/50	60 powder	4.0	1280	800		
417J[4]	Clad[5]	50/50	60 dust	6.0	1635	980	450	285
339J	Unclad	33/67	-	1.7	800	250		
365J	Unclad	33/67	60 powder	4.0	1190	740		
418J[6]	Clad[5]	33/67	60 dust	6.0	1445	935	275	325[8]
427J[7]	Clad[5]	33/67	60 dust	5.0	1415	620	155	105
432J[9]	Clad[5]	33/67	60 dust	5.0	1230	885		
340J	Unclad	25/75	-	3.8	1170	800		
363J	Unclad	25/75	60 dust	4.0	1275	1135		
419J	Clad[5]	25/75	60 dust	6.0	1225	755	75	70[10]

1) Flake aluminum powder, pigment grade, or aluminum dust (spherical particles) 84% finer than 325 mesh.
2) "Dicy" is dicyandiamide.
3) Average of three values for one-half inch lap joints; specimens 1.0 in x 0.064 in x 8.5 in.
4) Shear strength at 400°F: 1445 psi.
5) Length of test strips: 7.5 inches.
6) Shear strength at 400°F: 1315 psi
7) Formulation also contained 1 phr sodium glycolate.
8) Average of two values.
9) Formulation also contained 2 phr sodium glycolate.
10) One value; two test strips broke on handling.

Table 21. TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM A BLEND OF 50/50 EPON RESIN/PLYOPHEN 5023

Cure: oven-heating at contact pressure for one-half hour at 330°F.

Formulation No.	Aluminum Metal, 24S-T3	EPON Resin	Aluminum Dust, phr	Dicy,[1] phr	Tensile Shear Strength,[2] psi			
					Original		Aged 200 hrs. at 500°F	
					at 77°F	at 500°F	at 77°F	at 500°F
393J	Unclad[3]	834	60	4	1605	735		390
392J	"	864	"	"	2575	825	765	580
392J	Clad	"	"	"	2205	1040	480	415
496V[4]	"	"	100	5	2665	1265		
375J	Unclad[3]	Modified 864[5]	60	4	1835	615		
375J	Clad		"	"	2205	815	315	350
438J	"	Modified 864[6]	"	"	1685	1290		
372J	Unclad[3]	1001	"	"	2510	925	725	510
372J	Clad	"	"	"	1945	1240	330	305
406J	"	1004	"	"	1265	90		
370K[7]	Unclad[3]	1007	"	"	2685	335		
417J	Clad	X-12100	"	6	1635	980	450	285

1) "Dicy" is dicyandiamide.

2) Average of three values for standard test strips.

3) Length of test strip: 8.5 inches.

4) Precure: one-half hour at 200°F.

5) Experimental EPON resin LR922-82A.

6) Experimental EPON resin LR922-117A.

7) Cure: one hour at 330°F.

Table 22. TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM A BLEND OF 33/67 EPON RESIN/PLYOPHEN 5023

Cure: Oven-heating at contact pressure for one-half hour at 330°F.

Formulation No.	Aluminum Metal, 24S-T3	EPON Resin	Aluminum Dust, phr	Dicy,[1] phr	Tensile Shear Strength,[2] psi: Original at 77°F	Tensile Shear Strength,[2] psi: Original at 500°F	Tensile Shear Strength,[2] psi: Aged 200 hrs. at 500°F at 77°F	Tensile Shear Strength,[2] psi: Aged 200 hrs. at 500°F at 500°F
451J	Clad	828	60	6	1365	540		
452J	"	834	"	"	1390	585		
495V-1[3]	"	864	100	5	2070	1480	300[4]	105[4]
487V[3]	"	"	60	"	1615	1325		
374J	Unclad[5]	Modified 864[6]	"	4				
439J	Clad	Modified 864[7]	"	"	1350	1410	205[4]	85[4]
394J	Unclad[5]	1001	"	"	2285	1475	385	425[8]
394J	Clad	"	"	"	2275	1325	520	385
422J-3	"	"	100	6	2125	1400	305	215
418J	"	X-12100	60	"	1445	935	275	325[8]

1) "Dicy" is dicyandiamide.

2) Average of three values for standard test strips with one-half inch lap joints.

3) Precure: one-half hour at 200°F.

4) Aged 224 hours at 500°F.

5) Length of test specimen: 8.5 inches.

6) Experimental EPON resin LR922-82A.

7) Experimental EPON resin LR922-117A.

8) Average of two values; one specimen broke on handling.

Table 23. TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM A BLEND OF 25/75 EPON RESIN/PLYOPHEN 5023

Cure: Oven heating at contact pressure for one-half hour at 330°F.

Formulation No.	Aluminum Metal, 24S-T3	EPON Resin	Filler, phr	Dicy,[1] phr	Tensile Shear Strength,[2] psi			
					Original		Aged 200 hrs at 500°F	
					at 77°F	at 500°F	at 77°F	at 500°F
423J	Clad	828	20 asbestos 7TF2	4	1025	1060		
450J	Clad	828	60 aluminum dust	6	1445	705		
421J	Clad	834	60 aluminum dust	6	1210	815		
421J-1	Clad		60 aluminum dust	6	1545	940		
497V[3]	Clad	864	100 aluminum dust	5	1380	820		
497J	Clad	864	100 aluminum dust	5	2000	1605	280	205
368J	Unclad[4]	Modified 864[5]	60 aluminum dust	4	1755	1590		
368J	Clad	Modified 864[5]	60 aluminum dust	4	1665	1235	115	70
369J	Unclad[4]	Modified 864[5]	30 aluminum powder	4	1005	465		
440J	Clad	Modified 864[6]	60 aluminum dust	4	1530	1385	180	25
373J	Unclad[4]	1001	60 aluminum dust	4	1680	1550		
373P[7]	Unclad[4]	1001	60 aluminum dust		1970	1375	205	0
445J-27	Clad	1001	100 aluminum dust	5	1755	1380	300	375
419J	Clad	X-12100	60 aluminum dust	6	1225	755	75	0
371K[8]	Unclad[4]	1007	60 aluminum dust	4	2050	35		
376J	Unclad[4]	LR564-46-59		4	625	160		

1) "Dicy" is dicyandiamide.
2) Average of three values for standard test strips.
3) Precure: one-half hour at 200°F.
4) Length of test strips: 8.5 inches.
5) Experimental EPON resin LR922-82A.
6) Experimental EPON resin LR922-117A.
7) Precure: one-half hour at 290°F.
8) Cure: one-hour at 330°F.

Table 24. TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM COMBINATIONS OF EPON RESINS AND RESINOX 665

Cure: Oven heating at contact pressure for one-half hour at 200°F plus one-half hour at 330°F.

Formulation No.	Adhesive Formulation, parts by wt						Tensile Shear Strength, psi[1]	
	EPON Resin		Resinox 665	Aluminum Dust	Dicy[2]	Additive, phr		
	Grade	Amount					at 77°F	at 500°F
525V	828	50	50	-	-	-	1485	100
527V	"	"	"	-	-	0.05 rare earth naphthenate	1355	20[3]
526V	"	40	60	-	-	-	1275	45
528V	"	"	"	-	-	0.05 rare earth naphthenate	1350	115[3]
521V-3	"	30	70	-	-	-	925	410
522V	"	"	"	-	-	0.05 rare earth naphthenate	625	150[3]
553V[4]	"	"	"	60	-		940	585[5]
554V[6]	"	"	"	"	5		1065	295[5]
564V	"	"	"	"	"	5 Polyamide 100S	1110	255
562V	"	"	"	"	"	Polyamide 100S undercoat	1095	0
566V	"	"	"	"	-	5 copper acetylacetone	955	110
567V[7]	"	"	"	"	-	5 copper naphthenate	-	-
533V	"	"	"	-	-	100 acetone	855	30[3]
536V	"	33	33	-	-	34 Plyophen 5023	640	20[3]
531V	"	20	80	-	-	-	835	295
532V	"	"	"	-	-	50 acetone	515	105[3]
524V	"	10	90	-	-	-	480	-
529V	X-12100 828	42 16	42	-	-	-	1100	115[3]
534V	X-12100	42	"	-	-	16 Plyophen 5023	1135	190[3]
530V	"	50	50	-	-	-	795	110[3]
563V-1	1009	30	70	-	-	-	1170	395
572V	"	50	50	60	-		1795	125[3]
572Pr[8]	"	"	"	"	-	-	2375	200
571V	X-52100	30	70	"	-	-	805	410
537V	1001	33	33	-	3	34 Plyophen 5023	1135	140[3]
538V	"	"	42	-	-	25 Plyophen 5023	1075	365
540V	"	"	30	60	5	37 Plyophen 5023	1865	475
523V	-	-	100	-	-	-	475	305[3]

1) Average of three values for standard clad 24S-T3 aluminum alloy test strips. All breaks were adhesive type failures.
2) "Dicy" is dicyandiamide.
3) Average of two values; third specimen broke on handling.
4) Shear strength after 200 hrs at 400°F: 520 psi at room temperature; 835 psi at 400°F.
5) Tested at 400°F.
6) Shear strength after 200 hrs at 400°F: 585 psi at room temperature; 760 psi at 400°F.
7) Panel broke on handling.
8) Cured in press at 25 psi for one-half hour at 330°F.

Table 25. TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM COMBINATIONS OF EPON AND PHENOLIC RESINS

Cure: Oven-heating at contact pressure for one-half hour at 330°F.

Formulation No.	EPON Resin	Phenolic Resin	EPON/ Phenolic Resin Ratio	Aluminum Dust, phr	Dicy,[1] phr	Precure		Tensile Shear Strength,[2] psi				
								Original			Aged 200 hrs at 500°F	
						min	°F	at 77°F	at 400°F	at 500°F	at 77°F	at 500°F
360P[3]	X-12100	Lebec 102594	70/30	-	4	30	290	1070		190		
359P[3]	"	"	50/50	-	"	"	"	1285		50		
362P[3]	1007	"	70/30	-	"	"	"	945		25		
361P[3]	"	"	50/50	-	"	"	"	575		70		
357P[3]	X-12100	Plyophen 5015[4]	70/30	-	5	"	"	1060		75		
355P[3]	"	"	50/50	-	"	"	"	920		80		
358P[3]	1001	"	70/30	-	"	"	"	1495		45		
356P[3]	"	"	50/50	-	"	"	"	2135		215		
449J	"	"	33/67	60	4	-	-	1690		1275	215	120
463J	"	"	"	"	6	-	-	1870		1140	45	30[6]
479V	"	Plyophen 5015[5]	"	30	5	30	200	1405		470		
470W[7]	"	"	"	"	4	60	"	1055		375		
417J	X-12100	Plyophen 5023	50/50	60	6	-	-	1635	1445	980	450	285
442J-18	1001	"	33/67	100	"	-	-	2070		1600	80[8]	20[6]
549V	864	Resinox 618	30/70	-	-	30	200	2016	155			
550V	"		"	60	-	"	"	2590	110			
551V	"		"	-	5	"	"	1535	90			
552V	"		"	60	"	"	"	2095	110			

1) "Dicy" is dicyandiamide.
2) Average of three values for standard 24S-T3 clad aluminum alloy test strips.
3) Average of three values unclad 24S-T3 aluminum alloy test strips (1.0 in x 0.064 in x 8.5 in) with one-half inch overlaps.
4) Dehydrated in vacuo to a water content of 3.5%.
5) Dehydrated in vacuo to a semi-plastic state.
6) Average of two samples; third strip broke on handling.
7) Adhesive formulation also contained 2 phr sodium methoxide.
8) One value; two specimens broke on handling.

Table 26. TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM COMBINATIONS OF EPON 1001 RESIN AND SILICONE RESINS

Panel No.	Adhesive Formulation, parts by wt				Air Dry,[3] hrs	Precure[3] at 125°F, min	Cure at[4] 330°F min	Tensile Shear Strength,[5] psi	
	EPON 1001	Silicone Resin[1]	MEK[2]	Curing Agent				at 77°F	at 500°F
434J[6]	50	20 XR-398	50	7.5 hexa[7]	16	5	30	1725	265
434K[6]	50	20 XR-398	50	7.5 "	16	5	60	1960	275
435K	50	70 XR-261	50	2.5 DMP-30[8]	2	5	60	680	40
435	50	70 XR-261	50	2.5 "	2	5	120	1110	50
436K	70	65 XR-384	-	3.5 "	2	5	60	160	0
436	70	65 XR-384	-	3.5 "	2	5	120	500	10
437	50	110 XR-384	-	2.5 "	5	10	240	305	0

1) Dow Corning silicone resin.
2) MEK = methyl ethyl ketone.
3) Treatment of panel before assembly.
4) Oven heating at contact pressure.
5) Average of three values for standard clad 24S-T3 aluminum alloy test strips. All breaks were mainly adhesive type failures.
6) Formulation also contained 50 parts Plyophen 5023.
7) "Hexa" is hexamethylenetetramine.
8) DMP-30 is 1,3,5-tris-dimethylaminomethylphenol.

Table 27. TENSILE SHEAR STRENGTH OF ADHESIVE BONDS FROM EXPERIMENTAL EPON RESINS

Adhesive powders containing 5 phr dicyandiamide applied to panels preheated to 250°F

Cure: Oven-heating at contact pressure for one-half hour at 290°F plus one-half hour at 330°F

Formulation No.	EPON Resin	Variable	Tensile Shear Strength,[1] psi			
			at 77°F	at 300°F	at 400°F	at 500°F
343P	X-12100	10 phr polyadipic anhydride[2]	2350	--	--	220
267J[3]	"	30 phr aluminum dust[4]	2415	1400	530	385
297J[3]	"	Undercoat[5]	2015	1990	330	200
303J[3]	"	"	2185	1435	270	185
352P	Modified X-12100[6]	"	2290	--	--	200
353P	" "	--	1530	--	--	280
344P	70/30 X-12100/modified 864[7]	--	1765	--	--	275
345P	50/50 "	--	2490	--	--	270
346P	30/70 "	--	3030	--	--	170
337P	Modified 864[7]	--	2580	170	--	200
338P	" "	Undercoat[5]	4885	435	--	270
354P	864	--	4350	700	--	200
349P	X-42100[8]	Undercoat[5]	1955	--	--	210
350P	"	--	1410	--	--	385
312J[3]	LR564-46-59	--	4200	--	--	135
313J[3]	"	Undercoat[5]	625	--	--	160

1) Average of three values for 24S-T3 aluminum strips (1.0 in. x 0.064 in. x 8.5 in.) with one-half inch lap joints.
2) Resin precured with polyadipic anhydride for one-half hour at 250°F.
3) Cure: one-half hour at 330°F.
4) Adhesive used as pre-formed stick. Dicyandiamide concentration 4 phr.
5) Adhesive powder applied to an undercoat of <u>ca</u> 5 mils surfaced on the aluminum panel: EPON 834 + 8 phr Curing Agent A.
6) Experimental EPON resin LR922-87B.
7) Experimental EPON resin LR922-37.
8) Experimental EPON resin LR946-127.

Table 28. GENERAL PROPERTIES OF COMMERCIAL AND EXPERIMENTAL EPON RESINS

Grade	Type	Specific Gravity	Softening Pt. °F	Average Molecular Weight
828 [a]	Commercial	1.1676	48	355
834 [b]	"	1.1848	68-82	469
864 [c]	"	1.1881	104-113	710
1001	"	1.2041	149-167	900
1004	"	1.1194	207-217	1400
1007	"	1.1890	261-271	2900
1009	"	1.1890	293-311	3750
X-12100	Experimental		162	1060
LR-922-87B	Experimental: Modified X-12100		149	1081
LR-922-82A	Experimental: Modified 864		142	954
LR-922-117A	Experimental: Modified 864			716
X-42100	Experimental			835
X-52100	"			
LR 564-46-59	"		248	925

a) Formerly designated RN-48.

b) Formerly designated RN-34.

c) Formerly designated 1064.

Table 29. IDENTITY AND SOURCE OF MATERIALS EVALUATED IN HIGH TEMPERATURE ADHESIVE FORMULATIONS

Material	Description	Source
AgeRite Alba	hydroquinone monobenzyl ether	R. T. Vanderbilt Co.
AgeRite Powder	phenyl beta-naphthylamine	"
Aluminum dust	spherical particles, 84% finer than 325 mesh	General Chemical Division, Allied Chemical and Dye Corp.
Aluminum powder	flake; pigment grade	Aluminum Co. of America
Asbestos 7TF2	short fiber floats	Johns-Manville
Asbestos 7RF6	long fiber floats	"
Bentone 34	organophilic bentonite	National Lead Co.
Catalyst C	catalyst for EPON resin polymerization	Shell Chemical Co.
Celite 270	powdered silica filler	Johns-Manville
Celite, Filter-Aid	hydrated silicon dioxide	"
Copper naphthenate	solid form	Witco Chemical Co.
Curing Agent A	curing agent for EPON resins	Shell Chemical Co.
Curing Agent D	" " " " "	"
Dicyandiamide		American Cyanamid Co.
DMP-30	1,3,5-tris-dimethylaminomethylphenol	Rohm and Haas Co.
Duralon 31	furfuryl alcohol resin	U.S. Stoneware Co.
Fiberfrax	aluminum-silicate fiber	The Carborundum Co.
Fiber glass strands		Ferro Corporation
G.E. 12494	asbestos-filled Hycar rubber-phenolic molding powder	General Electric Co.
G.E. R108	modified phenol-formaldehyde resin	"
Hi-Sil	hydrated silicon dioxide	Columbia Southern Chemical Division, Pittsburgh Plate Glass Co.
Lebec 102594	high molecular weight phenol-formaldehyde novolac resin	Lebec Chemical Co.
Melmac 401	melamine-formaldehyde resin	American Cyanamid Co.
Plyophen 5015	liquid, one-stage phenol-formaldehyde laminating resin, 30% water	Reichhold Chemicals, Inc.
Plyophen 5023	liquid, one-stage phenol-formaldehyde casting resin, 15% water	Reichhold Chemicals, Inc.
Polyamide 100S	condensation product of dimerized fatty acids and diethylenetriamine	General Mills, Inc.
Pyrophyllite clay	hydrous aluminum silicate	
Rare earth naphthenate	polymerization accelerator	Advance Solvents and Chemical Co.
Resinox 618	grindable, one-stage phenolic resin, aniline-modified	Monsanto Chemical Co.

(Continued)

Table 29. IDENTITY AND SOURCE OF MATERIALS EVALUATED IN HIGH TEMPERATURE ADHESIVE FORMULATIONS (CONTD.)

Resinox 665	grindable, one-stage phenolic resin	Monsanto Chemical Co.
Silica gel	desiccant grade	Davison Chemical Co.
Silicone resin XR-261	70% solids in xylene	Dow Corning Corp.
Silicone resin XR-384	modified silicone resin (75% silicone), 45% solids in cyclohexanone	Dow Corning Corp.
Silicone resin XR-398	modified silicone resin, 50% solids in xylene	Dow Corning Corp.
Titanox RA	titanium dioxide	National Lead Co.